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Continental water balance, ground water inventory and storage times, surface ocean mixing rates and world-wide water circulation patterns from cosmic-ray and bomb tritium*

FRIEDRICH BEGEMANN and W. F. LIBBY†
The Enrico Fermi Institute for Nuclear Studies, University of Chicago, Chicago, Illinois

(*Received* 26 *November* 1956)

Abstract—The tritium produced during the Castle operation in the spring of 1954 has been used to study the circulatory rates for waters in the northern hemisphere, particularly in the northern Mississippi Valley. It is observed that northern hemisphere rains 6 months to 18 months following Castle had about half the tritium content that the surface water had, and this difference has revealed that about one-third of the rain in the Upper Mississippi Valley is ocean water and about two-thirds re-evaporated surface water. This allows the total inward transport of ocean water for the Upper Mississippi Valley to be calculated. It is about 1·0 m per year. It has been found that on the average tritium has a residence half-life of about 6 years on the continental land mass of North America (radioactive decay taken into account). This probably will be applicable to most other continental land masses. Water from the oceans stays in the northern Mississippi Valley 15 years on the average. The principal mechanisms by which ocean water deposited on the continents returns to the sea are in the rivers, and as moisture in air masses moving from the land to the sea where precipitation occurs. In the northern Mississippi Valley it is shown that on the average about 8 m of ground water or equivalent including bound hydroxyl groups in clays are available for mixing with the rainfall, about 0·28 m of water runs off annually in rivers, and 0·24 m per year are carried back to the oceans by the winds.

The atmospheric residence time of Castle tritium has been found to be about 40 days. So far no mixing of any "excess" tritium across the equator into the southern hemisphere has been noticed. The short stratospheric residence time of bomb-tritium as compared to bomb-fission products probably is due to the large amount of water taken into the fireball which condenses in the cold of the stratosphere to form the familiar cloud of relatively large water-drops or ice-crystals. These are large enough to descend more quickly than the finer fission product particles.

The cosmic-ray tritium production rate previously calculated to be 0·14 T-atoms/cm²/sec on the average now is thought to be too low, since the decay of tritium in groundwater and the amount by which the outward tritium vapour transport exceeds the inward flow from the seas are both now known to be important. The new value for $\overline{Q}$ is 1 T-atom/cm²/sec, as measured at the earth's surface, and 2 T-atoms/cm²/sec total, the difference being due to an assumed stratospheric residence time of 10 years on the basis of fission product fallout information. The direct measurement of tritium production cross-sections and calculation of $\overline{Q}$ from cosmic-ray intensities predicts that the average cosmic-ray production rate for tritium is about 0·14 T-atoms/cm²/sec averaged over the whole world, the intensity varying strongly with latitude about as the cosine of the latitude with a factor of 4 in intensity between the equator and the poles. The discrepancy may be due to an appreciable accretion of tritium directly from the sun, as suggested by J. R. ARNOLD and B. FELD. The new higher value for the production rate means that the world-wide inventory of cosmic-ray tritium is raised to about 30 kg from 1·8 kg, the upper limit to the escape time for ^{3}He from the atmosphere of the earth is about 2·5 million years.

Studies of the circulatory pattern of hot springs have shown that the waters of the several hot springs studied are rainwater that has been stored for relatively brief periods. Study of groundwaters has shown that in large areas the water issuing from wells dug for normal use is older than 50 years. It appears that the technique of studying the tritium content of well-water is quite likely to prove to be of real value in studying underground water supplies and in the prediction of their susceptibility to drought as well as depletion by pumping and the possibility of replenishment from rain or snow.

1. INTRODUCTION

IT HAS been clear from the beginning of the researches on the tritium produced by cosmic radiation (LIBBY, 1946; GROSSE *et al.*, 1951; FALTINGS and HARTECK, 1950) that the labelled water resulting from the production of tritium in the higher levels of the atmosphere would be of real usefulness (LIBBY, 1953). The initial results

* This research was supported by the office of Scientific Research of the Air Research and Development Command, Contract No. AF 18–(600)–564.

† Currently a member of the U.S. Atomic Energy Commission.

seemed to justify these expectations (KAUFMANN and LIBBY, 1954; VON BUTTLAR and LIBBY, 1955). It became clear, however, in the spring of 1954 that the tritium produced by the thermonuclear weapons tested in the Pacific constituted a new and abundant source larger than the cosmic rays themselves, and because of its placement in time was in some ways more useful for measurements of rates of natural water processes. For example, in Figs. 1 and 2, the enormous rise in the spring of 1954 in the assays of the rainwater in Chicago and in Ottawa (BROWN and GRUMMITT, 1956) was due to the Castle series of weapons' tests. Table 5 shows the integral amount of tritium deposited in various places in the northern hemisphere from this series.

2. ATMOSPHERIC STORAGE TIME FOR CASTLE TRITIUM

More than fifty samples of rain and snow, covering the period from 1 March 1954 to May 1956 have been collected in various places on the northern hemisphere and

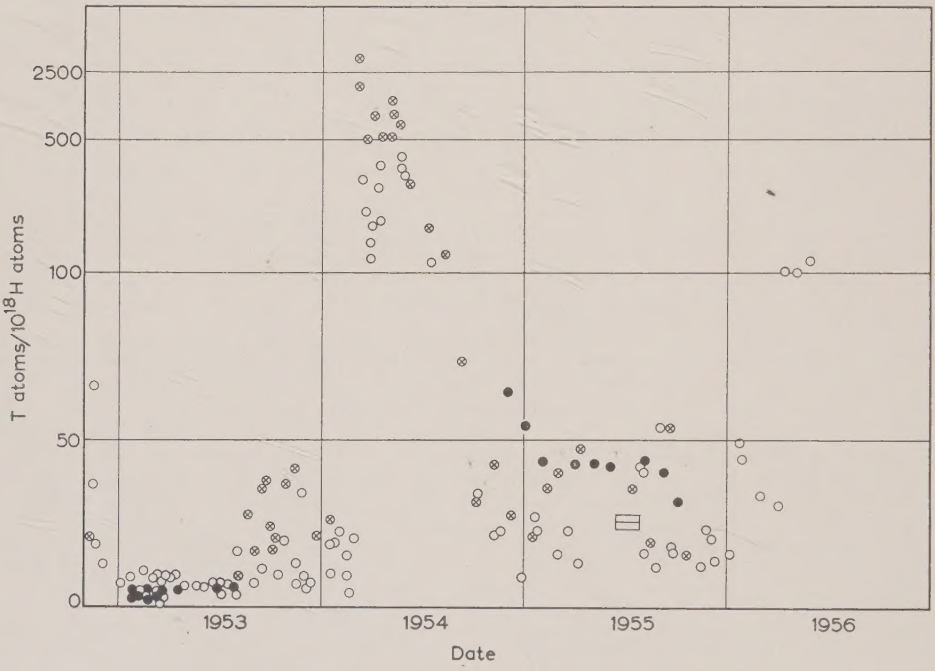

Fig. 1. Chicago and Ottawa rains and Mississippi River tritium contents.
○ = Chicago rain
⊗ = Ottawa rain
● = Mississippi

analysed for their tritium content. Figs. 1, 2, and 3 and Table 1 present the data obtained on these samples. (Table 1 contains the previously unpublished results only. Figs. 1 and 2 are complete (VON BUTTLAR and LIBBY, 1955). During the production period of the "excess" tritium in the spring of 1954 the results scatter widely. From June 1954 on, however, the tritium content decreases steadily, remains at a constant level for about one year, and starts to rise again at the beginning of 1956.

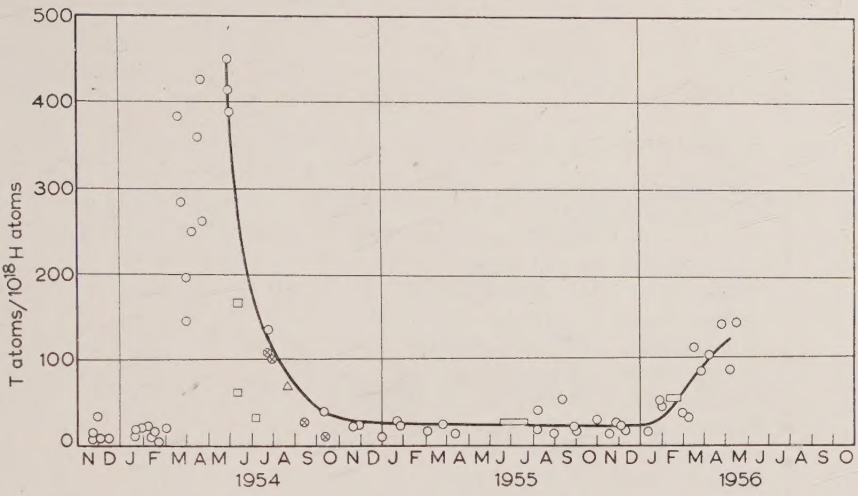

Fig. 2. Tritium content of rain and snow collected on Northern Hemisphere.
○ = Chicago
□ = Western Europe
⊗ = Mexico, New Mexico
△ = Greenland

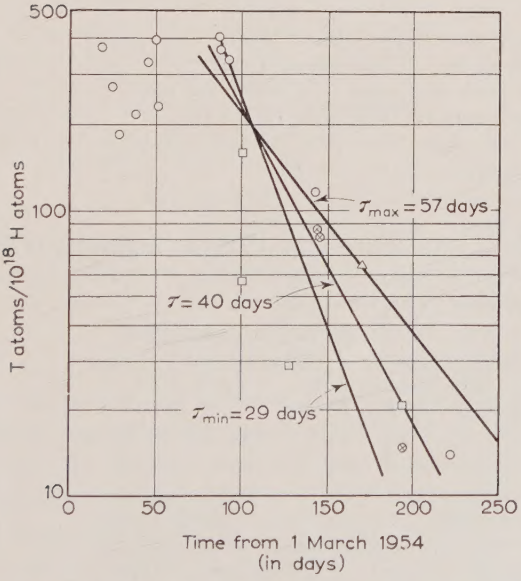

Fig. 3. Excess tritium in rains and snows on the Northern Hemisphere.
○ = Chicago
□ = Western Europe
⊗ = Mexico, New Mexico
△ = Greenland (Thule)

Table 1. Chicago and other rain and snow data

Sample no.	Description of sample	Tritium abundance (T atoms per 10^{18} H atoms)
181[a]	Chicago rain. 26–27 May 1954	450 ± 10
182[a]	Chicago rain. 27 May 1954.	416 ± 15
183[a]	Chicago rain. 1 June 1954	390 ± 5
206	Chicago rain. 20 July 1954	136 ± 10
245	Chicago rain. 9–10 October 1954	34·1 ± 1·5
232	Chicago rain. 21–22 November 1954	22·4 ± 1·2
235	Chicago rain. 24 November 1954	22·8 ± 1
242	Chicago snow. 29 December 1954	9·0 ± 1
243	Chicago snow. 20–21 January 1955	27·1 ± 1·5
244	Chicago snow. 24 January 1955	23·2 ± 1·5
255	Chicago rain. 3 March 1955	16·2 ± 0·8
259	Chicago snow. 22 March 1955	23 ± 1·2
263	Chicago rain. 11 April 1955	13·5 ± 0·7
332	Chicago rain. 5 August 1955	16·7 ± 1
331	Chicago rain. 14 June–25 July 1955. Sample represents aggregate of rainfall over this period.	26·0 ± 1·5
334	Chicago rain. 7 August 1955	41·0 ± 2
335	Chicago rain. 29 August 1955	12·3 ± 0·8
337	Chicago rain. 10 September 1955	54·0 ± 3
349	Chicago rain. 27 September 1955	18·0 ± 4
350	Chicago rain. 29 September 1955	17·0 ± 1
391	Chicago rain. 16 November 1955	12·5 ± 0·6
396	Chicago snow. 27 November 1955	24 ± 3
401	Chicago rain and snow. 2 December 1955	21 ± 2
402	Chicago snow. 9 December 1955	14 ± 2
403	Chicago rain and snow. 11 January 1956	16 ± 1·5
404	Chicago rain. 29 October 1955	30 ± 2
405	Chicago rain and snow. 28 January 1956	49 ± 3
406	Chicago snow. 1 February 1956	45 ± 5
412	Chicago snow and rain, aggregate from 6 February 1956 to 23 February 1956	53 ± 5
411	Chicago rain. 1 March 1956	34 ± 4
413	Chicago rain, thunderstorm. 5 March 1956	31 ± 3
414	Chicago heavy snow. 14 March 1956	112 ± 8
423	Chicago rain, thunderstorm. 6 April 1956	105 ± 10
426	Chicago rain. 25 April 1956	140 ± 10
	Unweighted average of 17 samples collected in Chicago covering 1955	23
224	Mt. Withington, New Mexico, rain. Aggregate of rainfall from 11 September–1 October 1954.	19 ± 1·4
234	Mt. Hood, Washington, snow. 1 October 1954	76·5 ± 4
237	Puebla, Mexico, rain. 8–10 September 1954	25 ± 1
238	Puebla, Mexico, rain. 12–13 October 1954	10·6 ± 0·5
249	Harwell, England, rain. 5 July 1954	32·5 ± 1·5

[a] VON BUTTLAR and LIBBY (1955).

Table 1 (*continued*)

Sample no.	Description of sample	Tritium abundance (T atoms per 10^{18} H atoms)
239	Thule, Greenland. Fell and collected, 17 August 1954	69·0 ± 3
286	Admiral Byrd Bay, snow; 69°34′S; 00°41′W; 1st ft. Collected 19 February 1955	24 ± 4
287	Admiral Byrd Bay, snow; 69°34′S; 00°41′W; 2nd ft.	12·5 ± 0·8
288	Admiral Byrd Bay, snow; 69°34′S; 00°41′W; 3rd ft.	13·5 ± 0·7
284	Admiral Byrd Bay, snow; 69°34′S; 00°41′W; 5th ft.	9·6 ± 1
285	Admiral Byrd Bay, snow; 69°34′S; 00°41′W; 6th ft.	5·2 ± 0·5
321	Antarctic snow; Atka Bay, 70°34′S; 08°06′W; 6 miles south of the edge of the Bay; collected 20 February 1955; top 8 in.	19·2 ± 0·8
306	Antarctic snow; ½ mile east of the Emergency Quonset at Little America III; collected 17 January 1955; top 8 in.	7·5 ± 0·6
310	Antarctic snow; ½ mile east of the Emergency Quonset at Little America III; collected 15 January 1955; top 8 in.	14·1 ± 1
323	Antarctic snow; snow pit near the Emergency Quonset at Little America III; collected 15 January 1955; 1–2 ft depth.	28·0 ± 1·5
324	Antarctic snow; snow pit near the Emergency Quonset at Little America III; collected 15 January 1955; 2–3 ft depth.	13·0 ± 0·5

It is clear from Fig. 2 that an airborne residence time* of about 40 days for the Castle tritium is indicated, in good agreement with the 50 day figure of Brown and Grummitt (1956). This is in sharp contrast not only with the 3 day figure for tropospheric moisture (von Buttlar and Libby, 1956), but also with the approximate 10 year figure for stratospheric fission products (Libby, 1956), particularly strontium-90 and caesium-137. It is close to the 32 day residence time for tropospheric fission products produced by the weapons fired in Nevada (Stewart *et al.*, 1956), though there is no apparent connection. Since the bomb clouds rose into the stratosphere, the rate corresponds most likely to the time of descent into the troposphere, where the much more rapid ordinary weather processes control with the shorter water residence time of perhaps 3 days. The water in the fireball condensed separately and in relatively large drops or crystals, because the Castle weapons vaporized enormous quantities of water and carried them into the stratosphere well labelled with the bomb tritium, which burned to water (measurements

* In this paper we use the term "residence time" to mean the time spent on the average when the fallout probability is the same for all particles, i.e. an exponential decay.

of atmospheric hydrogen collected at the earth's surface by the Linde Air Products Company both before and after Castle showed no increase over the previous cosmic-ray level). The particles of ice or supercooled water formed, therefore, were much larger than those containing the radio-strontium and radio-caesium and large enough to settle at this relatively rapid rate through the tropopause into the troposphere, where they melted and were precipitated as rain in 2 or 3 days.

Table 2 shows the tritium content of samples collected in the southern hemisphere following the Castle test series. None of these samples had a higher tritium content than similar ones collected in the northern hemisphere had before Castle, though the number of samples is small. This is in sharp contrast to similar data for the northern hemisphere as shown in Table 6. In particular, the samples representing the top layer of snow from the Antarctic did not show any increase in their tritium content over those from the 1–3 ft layer, the snow of which definitely fell before 1954. Thus, up until about one year after Castle there was no indication of any appreciable mixing of Castle produced tritium across the equator. This, of course, is in agreement with the short—40 day—time the Castle tritium spent in the atmosphere.

Table 2. Tritium content of samples from southern hemisphere

Sample no.	Location	Sample	Date of collection	T/H × 10^{18}
179	Valparaiso (Chile)[a]	Rain water.	4/4/54	4·3 ± 0·2
199	Livingston (S. Africa)	Zambesi River	May 1954	6·5 ± 0·2
260	Cape Province (S. Africa)	Berg River	Jan. 1955	2·8 ± 0·2
	Antarctic	Snow, top foot. Average of 4 samples. (Cf. Table 1.)	19/2/55	16 ± 3
	Antarctic	Snow, 1–3 ft layer. Average of 4 samples. (Cf. Table 1.)	15/1/55	17 ± 3

The Antarctic samples were collected in the coastal region, several miles inland.

[a] VON BUTTLAR and LIBBY (1955).

3. CASTLE TRITIUM DEPOSITION IN THE NORTHERN HEMISPHERE

In order to be able to make an estimate on the amount of "excess" tritium deposited per cm^2 in the northern hemisphere samples which were expected to be representative have been collected and measured. The results are given in Tables 3 and 4 and Fig 4.

In the case of the ocean water samples a thorough examination of the local oceanographic conditions for each of them will be necessary to explain the results

Table 3. Continental water samples (northern hemisphere)

Sample no.	Description of sample	Date of collection	T/H $\times 10^{18}$
	Crater Lake (Oregon)		
251	Surface	3/10/54	6·9 ± 0·3
252	1900 feet (bottom)	3/10/54	3·5 ± 0·5
340	Position 1, Surface	20/8/55	4·2 ± 0·3
341	1100 feet		6·0 ± 1
342	2000 feet (bottom)		7·6 ± 0·3
343	Position 2, Surface		4·7 ± 0·2
344	1200 feet		3·4 ± 0·3
345	1400 feet (bottom)		8·5 ± 1
346	Position 3, Surface		5·2 ± 0·5
347	550 feet		6·0 ± 1
348	1300 feet		9·5 ± 0·5
248	Lake Michigan, Surface, 2 miles off	8/2/55	10 ± 1
256	shore, 79th St., Chicago	10/3/55	7·3 ± 0·3
304		13/6/55	7·6 ± 0·4
223	Zurichsee (Switzerland), Surface	20/9/54	29·5 ± 1·5
264	Lake Tahoe (California), Surface	15/2/55	10 ± 0·8

in detail. These data are discussed in section 5 on "Surface Ocean Mixing Rates and Cosmic Ray Tritium Production Rate, $\bar{Q}$."

Here we use them only to estimate the amount of Castle produced tritium deposited per cm^2.

The results of the calculations for the total Castle tritium deposited in the northern hemisphere are given in Table 5.

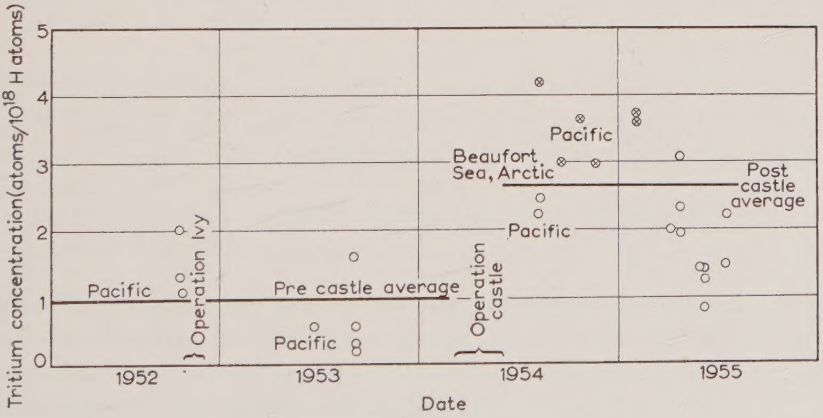

Fig. 4. Surface ocean water tritium. (Atlantic, unless labelled).
○ = Our data
⊗ = Brown and Grummitt

It is clear from Fig. 4 that the Castle tritium fallout raised the level in the surface ocean water by about 2 tritium atoms per 10^{18} hydrogen atoms on the average, and this figure is used in Table 5 together with a 75 metre average depth

Table 4. Ocean water samples (northern hemisphere)

Sample no.	Location	Depth	Date of collection	T/H × 10^{18}
	Atlantic (Sargasso Sea)			
219	36°04′N; 65°00′W	100 m	24/9/54	2·8 ± 0·1
220		200 m		1·33 ± 0·1
221		600 m		0·48 ± 0·05
	Atlantic			
282	43°17·5′N; 45°26′W	Surface	6/4/55	1·6 ± 0·2
280		42 m		2·2 ± 0·15
281		81 m		2·1 ± 0·1
	Atlantic			
290	49°01′N; 49°18′W	Surface	27/4/55	3·1 ± 0·2
291		62 m		3·25 ± 0·15
	Atlantic			
293	48°49′N; 48°07′W	Surface	28/4/55	1·6 ± 0·2
294		60 m		2·0 ± 0·1
295		120 m		1·1 ± 0·2
296		180 m		3·0 ± 0·2
	Atlantic			
297	48°28′N; 48°20′W	Surface	28/4/55	2·3 ± 0·15
	Atlantic			
360	55°01·5′N; 53°09′W	Surface	15/7/55	2·2 ± 0·2
361		56 m		0·40 ± 0·15
362		111 m		2·2 ± 0·2
363		170 m		0·60 ± 0·2
	Atlantic			
371	56°28·5′N; 50°30′W	Surface	17/7/55	1·3 ± 0·25
372		51 m		1·7 ± 0·2
373		85 m		2·4 ± 0·2
374		124 m		1·3 ± 0·15
	Atlantic			
375	52°03′N; 49°38′W	Surface	3/6/55	0·80 ± 0·05
376		58 m		1·2 ± 0·1
377		115 m		1·4 ± 0·2
378		171 m		1·2 ± 0·1
	Pacific			
257	37°38′N; 123°09′W	Surface	6/8/54	2·2 ± 0·1

of the thermocline in the ocean. The rise in assay of Lake Michigan (Table 3) was 5·6 T-atoms per 10^{18} H-atoms from 1·7 to 7·3, and when corrected for the contribution of the water drainage area which is about equal to the direct rainfall into the lake (HORTON, 1927) is about 50 per cent larger than that of the average ocean. Since Lake Michigan has an average depth of 95 metres (KAUFMANN and LIBBY, 1954) the effective average depths of mixing in the oceans would appear to be about 150 metres, somewhat more than but near the average depth of the thermocline, and possibly indicating some mixing below the thermocline. The data in Fig. 4, however, do not conclusively indicate a decrease in surface concentration with time, though the scatter is such that such decrease may be suggested by the

Table 5. Castle tritium deposition in the northern hemisphere

Location	Area of water body (sq. mile)	Drainage area (sq. mile)	Average depth (m)	Increase T/H 10^{18}	T-atoms/cm^2 C^2
Lake Michigan	22336	43148 (14·5/31·3 fractional run-off)	93	5·6	$187 \pm 20 \times 10^7$
Zurichsee (Switzerland)	34·2	770 (Assumed same fractional run-off as Lake Michigan)	45	26	67×10^7
Lake Tahoe (California)	193	1500 (Assumed same fractional run-off as Lake Michigan)	191	7	190×10^7
Crater Lake (Oregon)	19·3	Approx. 6	490	6	1800×10^7
North Atlantic and North Pacific	—	—	75*	2	100×10^7

* Average depth of thermocline

data. The mixing down to the thermocline apparently is rapid but is much slower beyond the thermocline.

The drainage of rainwater into Lake Michigan was assumed to take place before appreciable mixing with the groundwater reservoir took place. This assumption was made since the distances are small and the flow times correspondingly short. Since the information on drainage into Lake Tahoe and the Zurichsee was incomplete, it was necessary to estimate this contribution and accept the consequent uncertainty in the figures for the Castle tritium deposition in these lakes.

All of these data indicate that—with the exception of Crater Lake, where an abnormal behaviour might be expected because of its small size—there is fair agreement that as a result of Operation Castle about 200×10^7 tritium atoms were deposited on each cm^2 of the northern hemisphere (10^7 tritium atoms give 1 disintegration per min (Jones, 1955). Of course, the uncertainty in this number is large because of the limited number of data available.

4. Ground Water Inventory, Storage Times and Water Balance for the Northern Mississippi Valley

As a consequence of this deposition of "excess" tritium a remarkable increase in the tritium content of rivers and streams was noticeable. In Table 6 the results are presented.

For the samples collected in the United States later than January 1955 there is no marked dependence of the tritium content on the size of the rivers the samples come from. Therefore, for the following we shall take the Mississippi samples as representative for average continental water. The approximately 200×10^7 tritium atoms deposited per cm^2 of the northern hemisphere raised the tritium

Table 6. Post-Castle tritium content of rivers

Sample no.	Location	Date of collection	T/H × 10^{18}
231	Blue Nile, Khartoum (Sudan)	18/5/54	11·9 ± 0·5
230	White Nile, Khartoum (Sudan)	18/5/54	21·1 ± 0·5
222	Ticino (Switzerland)	24/9/54	40·5 ± 2
250	Aare, Berne (Switzerland)	30/12/54	16·0 ± 0·8
275		18/2/55	15·5 ± 0·8
300		15/4/55	13·5 ± 1·5
236	Mississippi	3/12/54	65 ± 3
246	Rock Island (Illinois)	3/1/55	55 ± 3
247		3/2/55	44 ± 2
254		1/3/55	40 ± 2
261		1/4/55	43 ± 3
289		4/5/55	43·5 ± 1
303		2/6/55	41·5 ± 1
333		1/8/55	44 ± 5
338		3/9/55	41 ± 2
351		1/10/55	32 ± 1·5
190	Steamboat Creek (Nevada)	20/7/54	280 ± 10
265		16/2/55	37·5 ± 2
270	Different sampling site	16/2/55	42 ± 3
267	Galena Creek (Nevada)	16/2/55	28 ± 1·0
189	Firehole River	15/7/54	205 ± 8
353	(Yellowstone Park, Wyoming)	17/9/55	36·2 ± 2
197	Gibbon River	14/7/54	170 ± 10
352	(Yellowstone Park, Wyoming)	17/9/55	28 ± 3

content by about 39 × 10^{-18} T/H from 4·7 (KAUFMANN and LIBBY, 1954; VON BUTTLAR and LIBBY, 1955) from 4·7 to 44 (in units of 10^{-18} T/H). Therefore, on the average about 7·7 metres of water or the equivalent amount of exchangeable hydrogen, part of which may have been bound to clay as hydroxyl groups, were mixed with the rain which carried down the Castle tritium in making up the river water, this amount being the average inventory for the Northern Mississippi Valley drainage area. This would be true, as pointed out to us by Professor W. J. Kaufman of the University of California, even if the mixing were incomplete, providing the rate of removal of water to the river does not vary appreciably with the amount of water above the contributing layer. This constancy of rate of contribution of water to the river with head of water above, or the completeness of mixing in the first few months, is supported by the constancy of the tritium concentration of the river water during the period of about 1 year following the Castle deluge. If the mixing had been only superficial, re-evaporation would have caused the rains to be richer in tritium than the river waters. Since the opposite was true, as shown in Fig. 1 and Tables 1 and 6, appreciable mixing must have occurred in a matter of a few months, and therefore it is likely that further mixing would have occurred during the next year had the mixing been incomplete.

At the same time that the tritium content of Mississippi water was at a nearly constant level of 44 × 10^{-18} T/H the rains and snows in the Chicago area showed a

rather constant tritium content of 21 $\times$ 10^{-18} T/H (see Figs. 1 and 2). This leads us to the conclusion that one-third of the average rainfall is re-evaporated water and two-thirds ocean water, since under the conditions obtaining during 1955 the tritium content of oceanic water vapour would have been about 2·5 $\times$ 10^{-18} T/H. (In this calculation correction is made for cosmic-ray tritium so just the bomb tritium is used. Thus 5 and 7 units are subtracted from the river and rainwater tritium contents, respectively.) As the average rate of annual precipitation is 0·77 m this means that per year about 0·52 m of ocean water and about 0·25 m of re-evaporated water rain out over the Upper Mississippi Valley as shown in Fig. 7. This conclusion, of course, is to be taken in the sense that Mississippi River water is defined to be typical of the water available for evaporation, a postulate that seems to be reasonable because incomplete mixing is hardly compatible with the constancy of the compositions of the rain and river waters.

The total of 0·77 metres annual precipitation must be balanced by re-evaporation and run-off water. In order to determine the net water balance for the Upper Mississippi Valley, we note that the annual run-off in rivers and streams, which is about 0·28 m, leaves 0·49 m per year as the average evaporation rate of groundwater. In order that this be only one-third of the air moisture, the winds must carry in about 1·0 m per year from the oceans of which 0·52 m precipitate as rain in the valley. The remaining 0·48 m together with 0·24 m of evaporated groundwater is carried by the winds back from the continent to the oceans. Thus the wind transport of ground water moisture from the land in the Northern Mississippi Valley back to the oceans is somewhat less than that carried by the Mississippi River, 0·24 m per year versus 0·28 m per year. These conclusions are displayed in Fig. 7.

It is interesting to compare these results, for the Northern Mississippi Valley with those for the whole North American Continent as obtained by Benton, Estoque, and Dominitz (1954) who measured the net inflow and outflow of water across the boundaries of the North American Continent during 1949. They obtained 0·91 m per year inflow, 0·76 m per year outflow in winds, and 0·15 m per year run-off. Of course, our data differ in giving a figure for the interchange between the air moisture and groundwaters, but the two sets show considerable agreement where comparable; for example, 1·0 m per year inflow and 0·72 m per year outflow, with the Mississippi playing an abnormally important role as return mechanism.

Concluding we can say: There appear to be the equivalent of about 8 m of groundwater which mix within a few months with rainfall in the Mississippi Valley, about 0·52 m of ocean water falls as rain per year, about 0·49 m per year re-evaporate, about 0·28 m per year drain off to the ocean from the rivers, and about 0·24 m of groundwater per year return to the oceans via the atmosphere. Thus, the average residence time of water in the Upper Mississippi Valley is about 15 years. This means that about 6·7 per cent of the Castle tritium is carried to the ocean and deposited each year—about 3·6 per cent being carried as river water and about 3·1 per cent as water vapour in the form of clouds and moisture in the air masses which are seaward bound where the water will be rained out as ocean precipitation. (In addition, of course, due to the radioactive decay 5·6 per cent of

the tritium disintegrates into ^3He each year, so the average expected life of the Castle tritium on the continental land masses will be about 8·2 years, with a half-life of 5·7 years.) Other areas will differ somewhat, though possibly not greatly in the amount of groundwater storage, atmospheric transport of water vapour and run-off in rivers. It seems not unlikely that the 6 year half-life figure for the persistence of the Castle tritium in the Northern Mississippi Valley may obtain rather widely. It will be most interesting to observe whether this is so.

5. Surface Ocean Mixing Rates and Cosmic-Ray Tritium Production Rate, $\bar{Q}$

The tritium contents of the surface ocean samples measured earlier were interpreted (von Buttlar and Libby, 1955) as indicating that the oceans do not mix below the thermocline in the average lifetime of tritium, 18 years. Further measurements are presented in Tables 4 and 7 and Fig. 4. Unfortunately our data on samples collected after Castle do not yet cover a time long enough that an appreciable decrease in the tritium content of the surface samples would enable us to calculate more accurately the average residence time of ocean water in the layers above the thermocline. They do indicate, however, that this time might be as short as 5 years.

These data, and the long ground water residence time of about 15 years, which is not negligible with respect to the average life of tritium as was assumed earlier (Kaufmann and Libby, 1954; von Buttlar and Libby, 1955) as well as the difference in the amount of tritium entering and leaving the continent as vapour

Table 7. Tritium content of pre-Castle ocean water samples (surface)

Sample no.	Location	Date of collection	T/H × 10^{-18}
	Atlantic		
314	44°00′N; 41°00′W	31/10/52	2·2 ± 0·25
314		Same sample as a check	1·8 ± 0·25
	Atlantic		
319	56°34′N; 51°01′W	22/10/52	1·3 ± 0·1
	Pacific		
320	27°41′N; 145°35′W	28/10/52	1·05 ± 0·1
320		Same sample as a check	1·0 ± 0·1
	Pacific		
315	33°04′N; 165°17′E	26/11/52	1·5 ± 0·2
	Pacific		
316	50°09′N; 144°31′W	19/12/52	16·3 ± 1
	Pacific		
318	09°00′N; 167°03′E	18/11/52	10 ± 1

Two of the samples have been measured twice as a check and to eliminate the possibility of having the samples contaminated during the processing. All results are corrected for radioactive decay.

which is more important than was realized formerly (VON BUTTLAR and LIBBY, 1955; CRAIG, 1956) and the probability of a stratospheric storage time of about 10 years (LIBBY, 1956), make it necessary for us to recalculate the mean production rate for the cosmic-ray tritium (KAUFMANN and LIBBY, 1954; VON BUTTLAR and LIBBY, 1955). In this connection it is interesting to note that the mean assays of tritium in the Mississippi Valley agree with those for wines which definitely were bottled prior to the firing of any thermonuclear weapons, when the tritium assays of the wines are corrected for radioactive decay (KAUFMANN and LIBBY, 1954; VON BUTTLAR and LIBBY, 1955). Furthermore, the assay of Lake Michigan, which was due to tritium deposited over the preceding 18 years, agrees well with the mean tritium content of rains during the year of 1953, considering the known hydrologic conditions of the Lake. It follows, therefore, that the tritium from Operation Ivy conducted in November 1952 was small in its contamination of the continental water masses as compared to that of Operation Castle, since otherwise these agreements probably could not have been obtained.

The value of $\bar{Q}$, the mean natural tritium production rate, neglecting for the moment the effect of stratospheric storage, is to be calculated by using the earlier data (KAUFMANN and LIBBY, 1954; VON BUTTLAR and LIBBY, 1955) but taking account of the groundwater storage time and the wind transport of continental groundwater to sea. If $\bar{Q}$ is the average production rate in the Northern Mississippi Valley (T-atoms/cm^2/sec), we calculate it to be:

$$\bar{Q} = \left(7{\cdot}7 \times 5 \times 10^{-18} \times \frac{0{\cdot}693}{12{\cdot}26} + 0{\cdot}72 \times 6 \times 10^{-18} + 0{\cdot}28 \times 5 \times 10^{-18} - 1{\cdot}00 \times 2{\cdot}5 \times 10^{-18}\right) \times \frac{100}{18} \times \frac{2 \times 6{\cdot}02 \times 10^{23}}{3{\cdot}15 \times 10^{7}}$$

where the first term is the radioactive decay in the groundwater reservoir, the second term is the wind borne outflow where the observed value of 8 for New York rain (Samples 148 and 149 of VON BUTTLAR and LIBBY [1955]) has been corrected to 6 for the expected fractionation of tritium in the condensation process (CRAIG, *et al.*, 1956) the third the run-off in the Mississippi, and the last term is the tritium brought in from the oceans bearing the tritium concentration found on the California coast. The result, 1·16 T-atoms/cm^2/sec, is not to be multiplied by the factor of 0·6 (KAUFMANN and LIBBY, 1954; VON BUTTLAR and LIBBY, 1955) used formerly to correct for the variation of the cosmic-ray intensity with latitude since the main part, the direct solar accretion as suggested in the next paragraph, probably should be uniform in intensity over the earth. This was pointed out to us by H. CRAIG. Finally, in addition, stratospheric storage for a period of perhaps 10 years in the average (LIBBY, 1956) leads to further correction to a total Q value of 2·0 which should probably be close to the world-wide average Q.

We note that direct measurements of tritium production cross-sections in the laboratory (FIREMAN, 1955; FIREMAN and ROWLAND, 1955; CURRIE *et al.*, 1956) have given lower results more nearly in agreement with the earlier $\bar{Q}$ value. This discrepancy may be due as suggested by J. R. ARNOLD, (1956) and B. FELD, (1956) independently to an appreciable accretion of tritium directly from the sun not

included in the earlier calculation. Therefore, it appears that we have determined $\bar{Q}$ the tritium production rate for natural tritium of either primary or secondary origin to be about 1 T-atom/cm²/sec at the earth's surface and 2 T-atoms/cm²/sec total with little variation with latitude to be expected (even if the entire production were by cosmic rays the long stratospheric storage time and completeness of stratospheric mixing indicated by the fission product data would be expected to reduce the variation with latitude to a minimum). The uncertainty in this value of $\bar{Q}$ probably is about 50 per cent. It is becoming clear that the opportunities for further measurements of $\bar{Q}$ are rapidly disappearing as man-made tritium becomes more abundant than the cosmic-ray product.

Craig (1957) had deduced from ^{14}C mixing rates for the sea that Q at the surface of the earth might well be as high as $1{\cdot}2 \pm 0{\cdot}5$ and that considering the stratospheric hold up $Q = 1{\cdot}7$ prior to learning of the results of this research. A Q value at the surface of 1 and a thermocline depth of 86 metres corresponds to an expected tritium content of surface ocean water of 1 T-atom/10^{18} H-atoms, if the mixing time for waters above the thermocline with the deeper water is taken very much longer than 18 years. This is an acceptable figure in view of the data in Fig. 4, several of which were taken before Operation Ivy, but the shorter storage times of perhaps 5 years deduced by Craig (1956) would reduce the expected surface tritium concentration but would not place it below the range of mixing times consistent with the experimental errors in Q and the tritium content of surface ocean water.

The consequences of the changes in both $\bar{Q}$ total and $\bar{Q}$ at the surface are important to both the steady state natural tritium inventory and the ^{3}He rate of escape from the earth too. The world-wide steady inventory of natural tritium rises from 1·8 kg (Kaufmann and Libby, 1954; von Buttlar and Libby, 1955) to 30 kg of which about one half is above the tropopause mainly as water of about 10^{-13} T/H ratio, and the average escape time (von Buttlar and Libby, 1955) for ^{3}He from the earth's atmosphere is reduced to about 2·5 million years.

6. Hot Springs

Several sets of samples from two main areas of thermal activity—Steamboat Springs, Nevada, and Yellowstone Park, Wyoming—have been analysed for their tritium content. The results are given in Tables 8 and 9.

In Figs. 5 and 6 the results are plotted together with those obtained on rain-water samples from the North American Continent.

Although recent measurements of H. Craig of the isotopic ratio D/H and O^{18}/O^{16} on water samples from these and many other springs from the same area have shown (Craig *et al.*, 1956) that all these waters most probably are of meteoric origin, nothing is known about the time it takes the water to come to the surface again. The few results given here do not allow us to answer this question completely. They show, however, that a detailed study of these problems with the use of tritium might very well help to solve them.

All results obtained up to now —except those on the samples from Vixen Geyser, Yellowstone Park and Spring no. 50, Steamboat Springs—can be explained by assuming that a small amount of recent rainwater shows up in these springs almost

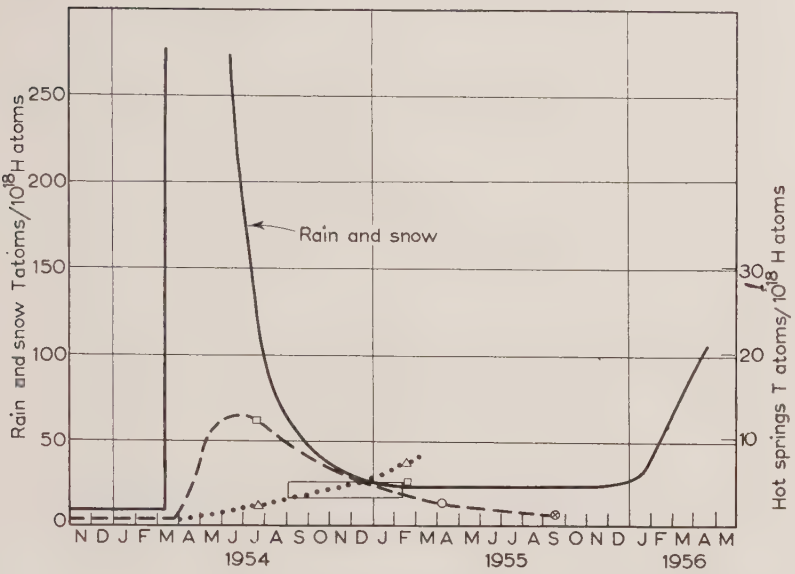

Fig. 5. Steamboat Springs, Nevada.
□ = South Steamboat Well
⊗ = Spring No. 16
△ = Spring No. 50

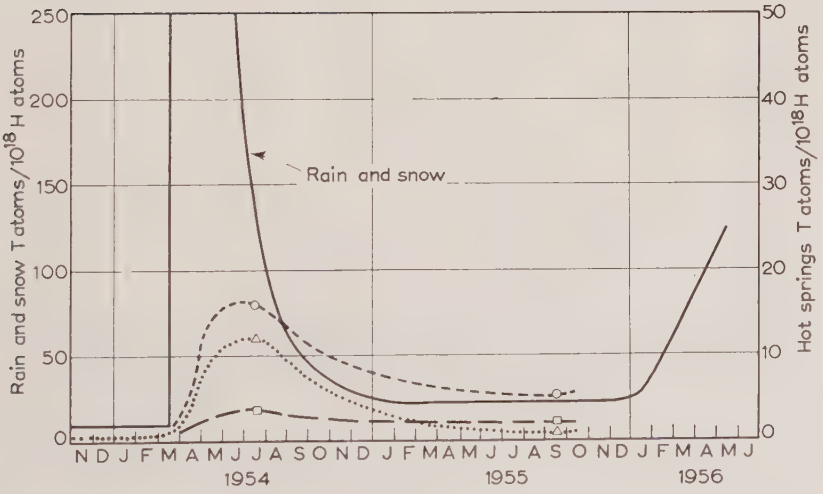

Fig. 6. Yellowstone Park, Wyoming.
○ = Hurricane Vent
□ = Ojo Caliente Spring
△ = Minerva Spring,

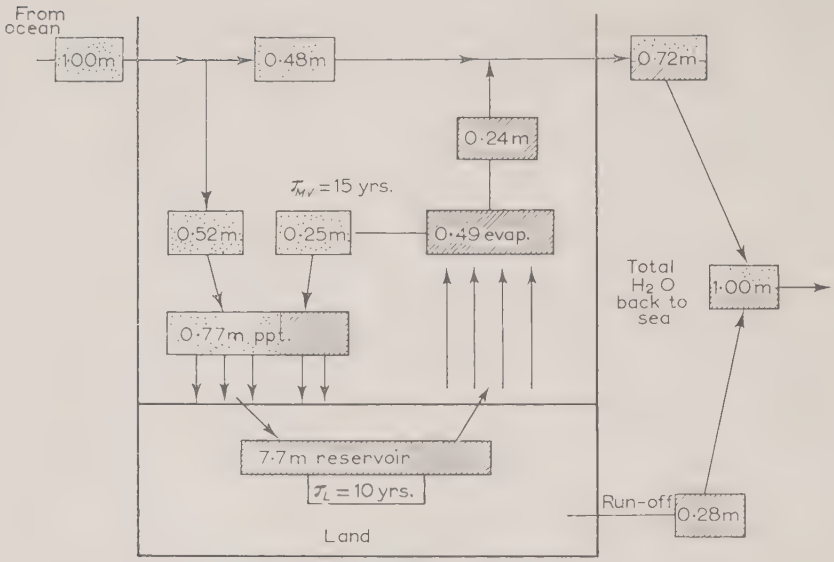

Fig. 7. Mississippi Valley water balance.

Table 8. Steamboat Springs, Nevada

Location	Date of collection	T/H × 10^{18}
South Steamboat Well	20/7/54	12·0 ± 0·9
South Steamboat Well	8/54–2/55	4·0 ± 1
South Steamboat Well	16/2/55	4·7 ± 0·5
South Steamboat Well	15/9/55	1·0 ± 0·2
Spring no. 50	20/7/54	2·5 ± 0·15
Spring no. 50	16/2/55	7·2 ± 0·2
Spring no. 16	5/4/55	2·3 ± 0·1
Spring no. 16	15/9/55	0·95 ± 0·1

immediately. The observed maxima of the tritium content show that complete mixing with the large body of groundwater has not yet taken place and that it may be a matter of years before a gradual increase in the tritium content of these springs becomes noticeable. Although the pre-Castle tritium content of all these springs is not known, the results on the set of samples collected in September 1955 certainly give upper limits. They allow us to estimate the "average age" of the main body of water to be about 50 years. ("Average age" is understood to be the age corresponding to the average tritium content and represents the time elapsed since the waters last fell as rain or snow.)

The amount of fresh rainwater in the Vixen Geyser seems to be somewhat larger than in the hot springs analysed here. Furthermore, there appears to be a delay of several months before this rainwater shows up.

A delay of about the same length of time seems to occur in the case of Spring

Table 9. Yellowstone Park, Wyoming

Location	Sample	Date of collection	T/H × 10^{18}
Norris Geyser Basin	Vixen Geyser	14/7/54	31·0 ± 1·5
		17/9/55	36·6 ± 1
	Vent near Hurricane	14/7/54	16·0 ± 0·8
	Vent	17/9/55	5·3 ± 0·3
Lower Geyser Basin	Ojo Caliente	15/7/54	3·75 ± 0·2
		17/9/55	2·1 ± 0·2
Upper Geyser Basin	Iron Spring	17/9/55	1·7 ± 0·1
	Artemisia Geyser	17/9/55	1·5 ± 0·2
Mammoth Hot Spring Terraces	Minerva Spring	16/7/54	12·1 ± 0·6
		17/9/55	1·1 ± 0·1

no. 50, Steamboat Springs. From the two measurements it is not clear whether the same type of "surface mixing" as suggested for the other hot springs takes place in this spring. The much smaller increase in the tritium content rather suggests the possibility that in this case the rainwater mixes more or less completely with the main body of groundwater before it comes to the surface again. This would explain the delay as well as the small influence of the very active rains.

This type of thorough mixing of the rainwater with the water in the main reservoir is even more obvious for another spring in a completely different area. Three samples from Wilbur Springs, Colusa County, California gave the results listed in Table 10.

Table 10. Wilbur Springs, Colusa County, California

Date of collection	T/H 10^{18}
23/3/54	1·0 ± 0·1
25/3/55	3·8 ± 1
9/11/55	5·5 ± 0·3

The possibility of a small maximum of the tritium content shortly after the appearance of bomb tritium in rains—indicating "surface mixing" as defined before—cannot be excluded from these three measurements. The interesting point, however, is that a gradual increase of the tritium content is already noticeable, indicating a rather fast mixing of rainwater with the main body of water representing the source of this spring.

Further measurements must be made before the curves for the tritium content vs. time (Figs. 5 and 6) can be taken seriously. Especially the position of the maxima is rather uncertain because of the few measurements that have been made on each individual spring.

Several springs in the Steamboat Springs area are now being collected regularly and will be measured to check the results given here.

7. Hydrological Applications

In co-operation with Dr. E. C. Reed of the University of Nebraska two sets of samples from selected wells in the state of Nebraska have been analysed for their tritium content. The results are listed in Table 11.

When the first set of samples was collected we had hoped that there might not yet be any contribution from Castle-produced tritium in these waters. This most probably is true for the Howard and York County samples, whereas for the one from Merrick County this possibility cannot be excluded.

Table 11. Nebraska Wells

Location of sampling site	Date of collection	T/H 10^{18}
Howard County Drilled well, depth 80 ft	28/10/54	$0{\cdot}44 \pm 0{\cdot}1$
Merrick County Drilled well, depth 44 ft	28/10/54	$2{\cdot}5 \pm 0{\cdot}2$
York County Drilled well, depth 155 ft	28/10/54	$0{\cdot}18 \pm 0{\cdot}03$
Same well	28/4/55	$3{\cdot}0 \pm 0{\cdot}2$
Seward County Drilled well, depth 130 ft	28/4/55	$2{\cdot}2 \pm 0{\cdot}2$
Seward County Drilled well, depth 100 ft	28/4/55	$1{\cdot}4 \pm 0{\cdot}4$
Clay County Drilled well, depth 100 ft	19/4/55	$1{\cdot}2 \pm 0{\cdot}1$

The main point of interest in these samples was not only their "average age" as defined above but the difference in the tritium content of the different samples as well, in order to determine the rate of groundwater movement or the rate of replacement of pore water by meteoric water. The sampling sites were chosen to provide as much information as possible. The area where the Howard County sample was taken is known to be an excellent infiltration area for groundwater. According to geological and hydrological evidence the ground water movement is fairly well known—this sample should have had the highest tritium content, the one from York County the lowest one. A high reading was expected for the Merrick County sample because of the relatively shallow water table in this area.

Our measurements on the first set of samples confirm this general picture, the

only exception being the unexpectedly low tritium content for the Howard County sample.

The results on the second set of samples—especially the one on the duplicate sample from York County—can be interpreted in two ways. These samples were collected in the spring, after a period of recharge of the groundwater reservoir and most probably came from a lesser depth than those collected in October, after a period of extensive use of the groundwater. As the water in a thick layer of aquifer does not necessarily have to have the same age throughout the whole layer, but may very well vary from youngest on the top to oldest at the bottom, this would explain our results without assuming any contribution from recent rains. The other possibility would be that again we do not have the simple case of just replacing pore water of a uniform age by meteoric water but rather a mixing of recent rainwater with old groundwater. This mixing would have to take place fairly close to the sampling sites. The results cannot be explained by assuming that this recent rainwater comes from the Howard County infiltration area: the time would be much too short. About 1 per cent recent rainwater mixed up with the groundwater would be sufficient to explain the increase in the tritium content we found. It does not seem impossible that such a small amount of rainwater mixes with the groundwater locally.

Again, further measurements must be made before a final answer can be given.

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Variations in isotopic composition of carbon from metamorphic rocks in northern Sweden and their geological significance

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Abstract—The $^{12}C/^{13}C$ ratio has been determined in 108 samples of graphites from metamorphic Pre-Cambrian and Caledonian sediments in northern Sweden. The aim of the investigation has been to ascertain if variations in the isotopic composition of carbon can contribute to a solution of petrogenetic problems when conventional petrographic methods fail. No correlation could be established between $^{12}C/^{13}C$ ratio on the one hand and degree of kineto-metamorphism, thermal or "regional" metamorphism on the other. It seems possible that at least some $^{12}C/^{13}C$ variations reflect fluctuations in the original sedimentary milieu, but nothing definite can be stated concerning the mechanism of isotopic fractionation in sedimentary processes.

Introduction

Ever since Nier and Gulbransen (1939) demonstrated the existence of considerable and significant variations in the proportions of the stable isotopes ^{12}C and ^{13}C in carbon of various origins, intense research work has been performed in various parts of the world on the isotopic composition of carbonaceous matter. The present investigation is connected with the work of a group in Stockholm engaged in these problems and it deals with carbon from Swedish Pre-Cambrian rocks. The purpose of the work was to find out if the isotopic composition of carbon can contribute to the elucidation of genetical problems of Pre-Cambrian geology. Since the rocks in question have been subjected to several kinds of transformations, the results must of course be considered in the light of present experience from younger rocks or recent carbonaceous matter and from the experimental and theoretical information on the fractionation of carbon isotopes. Several publications have been presented, which are of particular interest in this respect; for example, Rankama (1948a, 1948b); Wickman, Blix, and Ubisch (1951); Wickman (1952, 1953); Craig (1953, 1954a, 1954b); Landergren (1954); Jeffery, Compston, Greenhalgh, and de Laeter (1955). Certain differences in opinion still exist between various authors concerning the ultimate cause and mechanism of the fractionation process indicated by the variations in the isotopic composition of carbon in nature. Since the materials analysed in the present investigation are not likely to elucidate the fundamental causes of fractionation, the results will be considered mainly from a geological point of view. In the following it is examined whether any significant variations in isotopic composition in the rocks analysed exist, if the variations are in agreement with those of corresponding rocks in younger systems, and if the variations can be connected with characteristic features of the individual rocks, as indicated by field mapping and conventional petrographic methods.

Both graphites and carbonates, mainly from metamorphic limestones or dolomites, have been analysed. The same general difference between carbon in

carbonate and graphitic carbon as has been observed by previous workers on this subject (see references above) were found to exist in the present material. The variations in the isotopic composition of the carbonate will, however be discussed in detail in a sequel to this work.

The preparation of the samples for analysis was performed by A. Parwel. The conversion of graphite carbon to barium carbonate was carried out by the method given by A. Parwel in an appendix to a paper by Landergren (1954).

The mass spectrometric measurements were performed by Mr. R. Ryhage at the Department of Chemistry of Karolinska Institute, Stockholm. The reproducibility of the results is estimated to $\pm 0{\cdot}05$ unit in most cases.

Brief account of the geological features of the Pre-Cambrian areas considered

The Pre-Cambrian specimens analysed derive from the two northernmost provinces in Sweden, Vesterbotten County and Norrbotten County, the Pre-Cambrian parts of which together comprise 118.000 sq. km or 26 per cent of the total area of Sweden. These regions were considered suitable for several reasons, namely: (1) Graphite-bearing sediments and, to a certain extent, limestones, are fairly common and widely distributed; (2) highly varying grades of regional metamorphism are represented in supracrustal rocks from various parts of the area; (3) recent mapping has made modern geologic maps of the areas in question available (the present author wrote the description to the map of Vesterbotten County (Gavelin, 1955) and is consequently personally acquainted with the geology of this area and, from excursions and some field work, also with the geology of the Norrbotten area); (4) preliminary work on carbon isotopes presented by Rankama (1948a) and Mars (1951) indicated some very interesting divergencies between certain graphite-bearing schists from northern Finland and Sweden with respect to their $^{12}C/^{13}C$ quotients as compared with corresponding rocks from other areas. If these divergencies should prove to be constant and significant for a certain rock sequence, they would be of great importance for the identification of various rock series in these areas.

Plutonic rocks, mainly of granitic composition, occupy a considerable portion of the area, but volcanites, varying from rhyolitic to basaltic composition, and normal sediments also occur. Sometimes the supercrustal rocks are but slightly metamorphosed with well-preserved primary textural and structural features in both lavas and sediments. On the other hand, originally analogous rocks may have been changed to schists, gneisses, or even to granitic rocks by regional metamorphism. Folding and shearing have sometimes intensely affected the structural features. In the northern part of the Vesterbotten area a fairly regular arrangement of various metamorphic zones can be discerned, which makes it possible to draw certain isograds for metamorphism over large areas. The gneisses in this area can generally be characterized as "veined gneisses," viz. heterogeneous rocks containing a certain amount of pegmatitic material; they represent in most cases highly metamorphosed sediments.

In Vesterbotten three main areas characterized by different distribution and development of the rocks can be distinguished. In the north, both sediments and volcanites occur. Granites are also present, but regional metamorphism is of low

grade over large areas and the primary structural and textural features are frequently well preserved. The south-eastern part of Vesterbotten is dominated by veined gneisses with subordinate granite masses. Finally, the south-western areas are characterized by the prevalence of fairly homogeneous porphyritic granites with subordinate belts or irregularly-shaped masses of schists, which are frequently graphitic, and sometimes transformed to gneisses (see Fig. 1).

Two different cycles of rock evolution are assumed to have occurred. The Vesterbotten rocks analysed all belong to the older (Svecofennian) cycle; the Norrbotten rocks, on the other hand, belong mainly to the younger (Karelian) cycle. The oldest rocks probably date back 2000 million years or more.

The limestones from the Vesterbotten area form a persistent bed below a very thick series of sediments where argillaceous or fine-grained arenaceous rocks are prevalent. They are generally feldspathic, poorly sorted, and can be characterized as typical members of the greywacke series (according to PETTIJOHN'S nomenclature (1949)). In this sedimentary series graphite- and sulphide-bearing schists (sometimes slates) are abundant. The material for analysis from the Norrbotten area was obtained from sediments partly similar to the Vesterbotten type. In some cases, however, the sedimentary sequence contains appreciable amounts of quartzites and limestones associated with argillaceous sediments; these may contain graphitic beds.

The primary source of the graphite carbon

RANKAMA (1948b) stated that the isotopic composition of graphites from Archaean schists and slates indicates an organic origin of the carbon in the sediments. This conclusion has been criticized by CRAIG (1954a, 1954b), who argues that since the fractionation of isotopes connected with graphitization cannot be considered in terms of thermodynamical data, the isotopic composition cannot be employed as an indicator of the primary source of the carbon. In his latest contribution to this discussion, RANKAMA (1954) stresses the geological evidence for an organic origin of the graphite in Pre-Cambrian sediments and gives a survey of arguments presented by various geologists in favour of such interpretations.

Regarding the graphites analysed in the present investigation, geological evidence seems to the author to be in favour of an organic origin. The appearance of the graphitic rocks with preserved sedimentary features, their facies developments, and their quantitative distribution in the sedimentary column makes them so similar to sediments of younger age that agreement with respect to genesis can hardly be doubted. Thus, for example, graphitic rocks corresponding to those of the Pre-Cambrian areas of Vesterbotten and Norrbotten occur in the Cambro-Silurian sediments of the Caledonian mountains, which in low-metamorphic areas appear as bituminous shales, the alum shales being one well-known type. If these last-mentioned sediments are taken to represent sapropelic accumulations, a similar origin for the Pre-Cambrian sediments must certainly be postulated. Since the gneisses can be shown by field evidence to come mainly from sediments, a similar origin of the graphite in the gneissose regions must be concluded. Moreover, the graphite in the gneisses generally occurs in narrow bands, which in some places have been traced by geophysical measurements for thousands of metres. In the

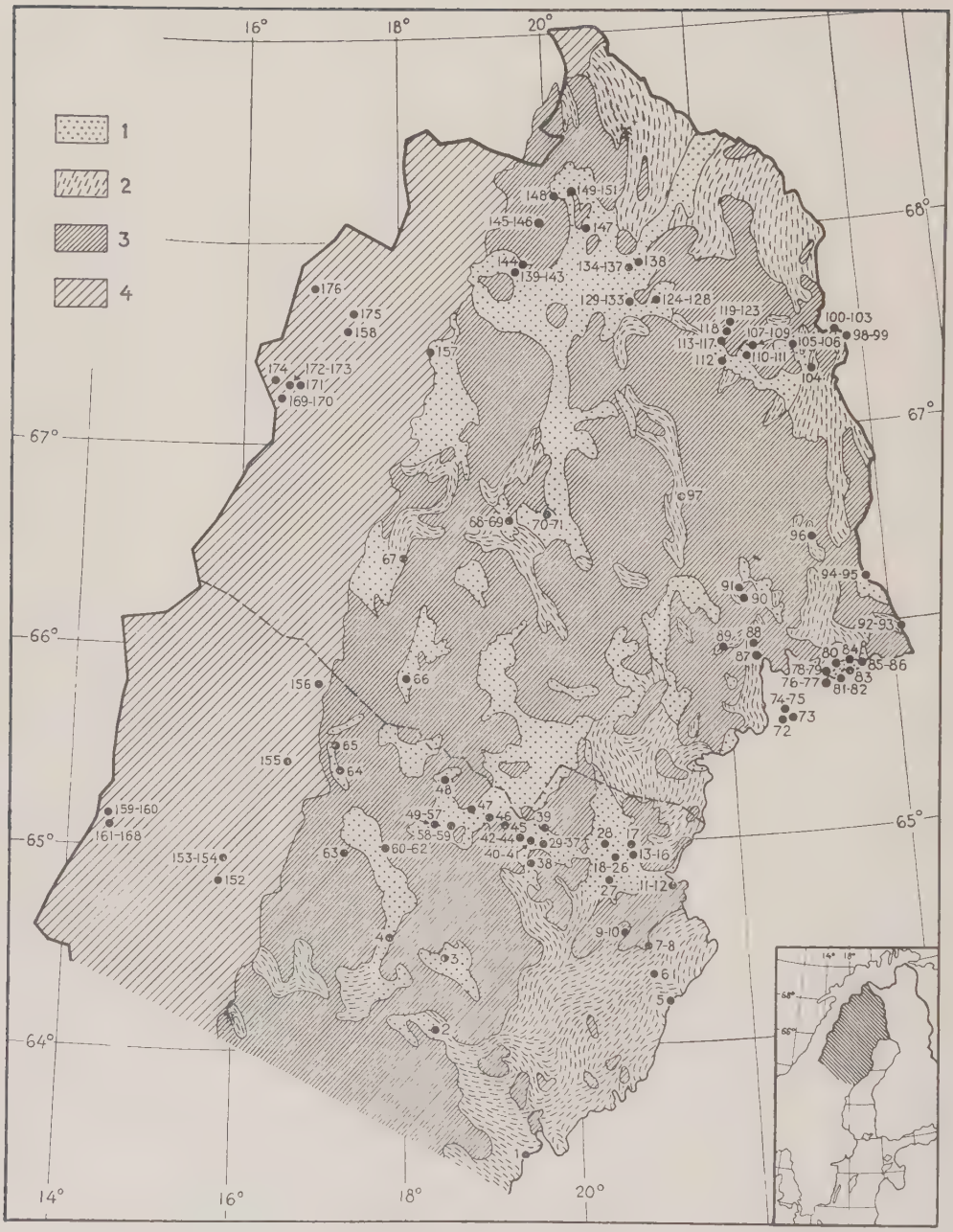
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Fig. 1.

present investigation it has therefore been assumed on the basis of geological considerations that the source of the carbon of the graphite analysed is similar in origin to that of the carbon in certain younger bituminous sediments.

The material analysed and presentation of the results

Fig. 1 gives a survey of the location of the samples analysed. This map demonstrates all localities from which material for the analyses were gained, graphitic rocks as well as carbonate rocks. Most of the samples from the Vesterbotten area and some of the Norrbotten samples were collected by the author, a series of samples from one drill hole in Vesterbotten was furnished by Dr. E. Grip, Chief Geologist of the Boliden Mining Company. The majority of the Norrbotten samples were selected under the guidance of Prof. O. Ödman, Royal Institute of Technology, Stockholm, and Dr. T. Eriksson, Geological Survey of Sweden. The Caledonian samples were given me by Dr. G. Kautsky, Geological Survey of Sweden. The geologists who placed the samples at my disposal kindly furnished information about the geological characteristics of those localities unknown in detail to me.

As far as possible the samples were chosen to represent vertical and lateral variations in a sedimentary rock sequence, in facies development of the sediments and in degree of metamorphism. Since the various types of Archaean rocks (granites, gneisses, volcanites, and sediments) have a very irregular areal extension in the regions examined, it is evident that the localities from which the samples were collected must also be irregularly situated. Sometimes continuous beds of phyllites and limestones can be followed in the field for tens or hundreds of miles. On the other hand, isolated areas with recognizable volcanic or sedimentary structures are separated by very wide areas of granites or gneisses. This means that it has frequently been convenient to make a certain grouping of the samples according to their mutual positions in the field, or, where possible, according to their tectonic positions.

An important point in the present investigation has clearly been to demonstrate the range of variation of the analyses within a defined portion of a sedimentary mass. Several samples from one locality may yield such information, and generally samples from drill holes are best suited for this purpose. In many cases, however, it is difficult to deduce the relative positions of the samples in the unfolded sedimentary beds even when they were taken within a quite small area or from the same "locality." In spite of this, it will be shown below that even grouping on merely tectonic or spatial grounds may be illuminative.

Reproduction of data

Table 1 gives a survey of all graphites analysed. Eighty-three samples of Pre-Cambrian rocks, and twenty-five samples of Cambro-Silurian rocks from the Caledonian mountain range (see Fig. 1) have been analysed. In order to make the results directly comparable with the values published by Craig (1953, 1954a, 1954b) and Jeffery *et al.* (1955), the values of the present investigation, given as the quotient $^{12}C/^{13}C$ on the Stockholm scale, were also converted to δ-values referring to the Chicago scale and, conversely, the δ-values of Craig and Jeffery *et al.* were converted to the $^{12}C/^{13}C$ ratio on the Stockholm scale. Both kinds of

Table 1. Survey of all analyses of graphitic rocks in the present investigation (Samples from the same "locality" have been denoted by the same small letter, *a* to *l*, after the sample number)

Number on the map Fig. 1		$^{12}C/^{13}C$	δ
	Gneiss areas in Vesterbotten		
1	Graphite-gneiss with sulphides	90·71	−23·3
5	Graphite-bearing gneiss	91·11	−27·6
6	Graphite accumulation in gneiss	90·45	−20·6
7	Gneiss with flakes of graphite	90·42	−20·3
	Granite-schist areas in Vesterbotten		
2	Graphite-schist, slightly arenaceous	91·13	−27·9
3	Graphite-schist with sulphides	90·61	−22·3
4	Graphite-schist, sulphide-bearing, fine-grained	91·11	−27·7
60	Phyllitic graphite-schist	91·02	−26·8
61	Graphite-schist with sulphides	91·50	−31·9
62	Graphite-schist with abundant sulphides	91·13	−27·9
63	Graphite-schist	90·44	−20·5
64	Phyllitic graphite-schist	91·11	−27·7
65	Graphite-schist	91·31	−29·9
	Skellefte district, Vesterbotten		
15	Graphite-schist with sulphides	91·12	−27·8
17	Graphite-schist	90·96	−26·1
	Drill hole "Strömfors 3"		
19	*a* Graphite-schist, fine-grained, phyllitic	90·86	−25·0
20	*a* Graphite-schist, fine-grained, phyllitic, sulphide-bearing	90·79	−24·3
21	*a* Graphite-schist, fine-grained, phyllitic, sulphide-bearing	90·95	−26·0
22	*a* Graphite-schist, fine-grained, phyllitic, veinlets of sulphides	90·98	−26·3
23	*a* Graphite-schist, fine-grained, phyllitic	90·87	−25·1
24	*a* Graphite-schist, fine-grained, phyllitic	90·91	−25·6
25	*a* Graphite-schist, fine-grained, phyllitic	91·11	−27·7
26	*a* Graphite-schist, fine-grained, phyllitic	91·08	−27·3
27	Graphite-schist with cordierite and andalusite	90·85	−24·9
28	Platy phyllitic graphite-schist	90·64	−22·7
29	Contact-metamorphic graphite-schist	90·82	−24·7
30	Graphite-schist with veinlets of sulphides	91·22	−28·9
	Drill hole "Rutselheden 4"		
32	*b* Dense graphite-schist	90·89	−25·3
33	*b* Dense graphite-schist	90·87	−25·1
34	*b* Dense graphite-schist	90·91	−25·5
35	*b* Dense graphite-schist	90·91	−25·5
36	*b* Dense graphite-schist	90·86	−25·0
37	*b* Dense graphite-schist	90·88	−25·2
38	Graphite- and cordierite-bearing gneiss	91·02	−26·8
39	Graphite-phyllite with graded bedding	91·40	−30·8

Table 1—*continued*

Number on the map Fig. 1			$^{12}C/^{13}C$	δ
		Skellefte district, Vesterbotten—contd.		
		Skäggträskberget		
40	*c*	Crumpled phyllitic graphite-schist with sulphide veinlets	90·40	−20·1
41	*c*	Phyllitic graphite-schist	90·35	−19·6
42		Quartz-phyllitic graphite-schist	90·42	−20·3
45		Graphite-schist with quartz veinlets	90·94	−25·9
46		Phyllitic graphite-schist	91·21	−28·8
47		Phyllitic graphite-schist	90·71	−23·4
48		Phyllitic graphite-schist	91·30	−29·8
		Drill hole "Rävliden 1"		
50	*d*	Phyllitic graphite-schist with arkosic layers	90·81	−24·5
51	*d*	Phyllitic graphite-schist with calcite veinlets	90·78	−24·2
52	*d*	Phyllitic graphite-schist with quarzite beds	90·79	−24·3
53	*d*	Phyllitic graphite-schist	90·81	−24·5
54	*d*	Phyllitic graphite-schist with layers of quarzite	90·67	−23·0
55	*d*	Phyllitic graphite-schist with veinlets of sulphides and quartz	90·74	−23·8
56	*d*	Phyllitic graphite-schist with abundant sulphides veinlets	90·74	−23·8
57		Graphite concentration on fault plane	90·55	−21·7
58		Fine-grained quarzitic graphite schist	91·04	−27·0
59		Phyllitic graphite-schist with sulphides	90·84	−24·8
		Gneiss and granite-schist areas in Norbotten (South-eastern areas, moderate or low regional metamorphism)		
72		Coarse-grained graphite-schist with sulphides	91·10	−27·6
73		Crumpled graphite-schist with sulphides	90·95	−26·0
84		Coarse graphite-schist with sulphides	90·73	−23·6
		(South-eastern areas, gneiss metamorphism)		
88		Graphite-schist with veinlets of quartz and sulphides	90·56	−21·8
89		Graphite-schist	90·72	−23·5
90		Graphite-schist	90·95	−26·0
91		Graphite-schist, slightly gneissic	90·34	−19·4
		Armasvaara		
94	*e*	Graphite-bearing gneiss	90·76	−24·0
95	*e*	Graphite-bearing gneiss	90·66	−22·9
96		Graphite accumulation in veined gneiss	90·50	−21·1
97		Graphite-bearing gneiss	91·13	−27·9

Table 1—*continued.*

Number on the map Fig. 1		$^{12}C/^{13}C$	δ
	Graphite-schists in Northern Norrbotten		
	Ristimela		
98	*f* Graphite accumulation in graphite-schist	90·15	−17·3
99	*f* Graphite-schist	90·18	−17·7
	Huuki		
100	*g* Graphite-schist	90·80	−24·3
101	*g* Graphite-schist	90·60	−22·2
105	Graphite accumulation in graphite-schist	91·21	−28·8
112	Graphite accumulation in graphite-schist	90·34	−19·4
118	Graphite accumulation in graphite-schist	90·51	−21·2
	Drill hole "Meraslinka 2"		
119	*h* Coarse, platy graphite in graphite-schist	90·95	−26·0
120	*h* Coarse, platy graphite in graphite-schist	90·89	−25·3
121	*h* Coarse, platy graphite in graphite-schist	90·80	−24·4
122	*h* Coarse, platy graphite in graphite-schist	90·70	−23·3
123	Graphite-schist	90·51	−21·2
124	Graphite-schist, crumpled, sulphide-bearing	90·40	−20·1
125	Graphite-layers in graphite-schist	90·32	−19·2
	Aijärova		
126	*i* Graphite accumulation in graphite-schist, skarniferous	90·63	−22·5
127	*i* Graphite accumulation in graphite-schist, skarn-bearing	90·32	−19·2
	Svappavaara		
129	*j* Graphite-schist with sulphide impregnation	90·79	−24·3
130	*j* Graphite accumulation in graphite-schist	90·94	−25·9
	Läppäkoski		
136	*k* Graphite-schist with spots of quartz, skarn minerals, and sulphides	89·97	−15·4
137	*k* Graphite-schist	91·04	−27·0
	Metamorphic bituminous sediments from the Caledonian mountains of Sweden		
	(Eastern border facies)		
152	Graphite-phyllite	91·06	−27·2
153	Graphite-phyllite	91·07	−27·3
154	Graphite-phyllite	91·08	−27·4
155	Graphite-phyllite	91·17	−28·2
156	Graphite-phyllite	91·13	−27·9
157	Graphite-phyllite	90·99	−26·4
158	Graphite-phyllite	91·13	−27·9

Table 1—*continued*

Number on the map Fig. 1		$^{12}C/^{13}C$	δ
	Metamorphic bituminous sediments from the Caledonian mountains of Sweden—contd.		
	(Eastern border facies from the inner part of the Caledonian belt)		
159	Graphite-schist	90·70	−23·3
160	Graphite-schist	90·73	−23·6
	(Western facies)		
	Drill hole "Stekenjokk 23"		
161	*l* Graphite-schist	90·45	−20·6
162	*l* Graphite-schist	90·45	−20·6
163	*l* Graphite-schist	90·53	−21·5
164	*l* Graphite schist	90·78	−24·2
165	*l* Graphite-schist	90·78	−24·2
166	*l* Graphite-schist	90·52	−21·3
167	*l* Graphite-schist	90·85	−24·9
168	*l* Graphite-schist	90·85	−24·9
169	Graphite-schist	90·73	−23·6
170	Graphite-schist	90·76	−24·0
171	Graphite-phyllite	90·85	−24·9
172	Graphite-schist	90·39	−20·0
173	Graphite-schist	90·67	−23·0
174	Graphite-phyllite	90·96	−26·1
175	Graphite schist	90·82	−24·6
176	Graphite-phyllite	90·61	−22·3

values are presented in Table 1 and in the diagrams. According to a new calibration, kindly performed by Dr. H. CRAIG, the Stockholm standard is $\delta = -10{\cdot}33$ on the Chicago scale. Conversely, the Chicago standard is 88·585 on the Stockholm scale. In accordance with CRAIG's directions, the analyses of shales, slates, and schists given in his paper (1953) have also been corrected for the difference in ^{17}O between the standard and the gas in the spectrometrically examined carbon dioxide by the addition of $\delta = +0{\cdot}5$ to his δ-values.

In a following paragraph, the analyses are presented *inter alia* in diagrams, giving a survey of the distribution of data. In Fig. 2(a) each square in the diagram represents one analysis. For a survey of the frequency of certain $^{12}C/^{13}C$ values in the rocks examined, this type of diagram is, however, not quite satisfactory. If the samples analysed are grouped according to spatial occurrence and if the ranges of variation within the individual groups are fairly small as compared with the variations in the entire material analysed (which will be shown is generally the case), it is evident that in diagrams with one analysis taken as unit, certain values may be particularly frequent owing to the fact that they are represented by several analyses from one "locality" with fairly constant isotope ratios. Since one "locality"

may be represented by one single analysis, another by two or more analyses, etc., the "locality" has been taken as unit, and consequently one analysis from a drill-hole with seven analysed samples is given the height of one-seventh of a square in the second type of diagram (Fig. 2b). From a statistical point of view this is

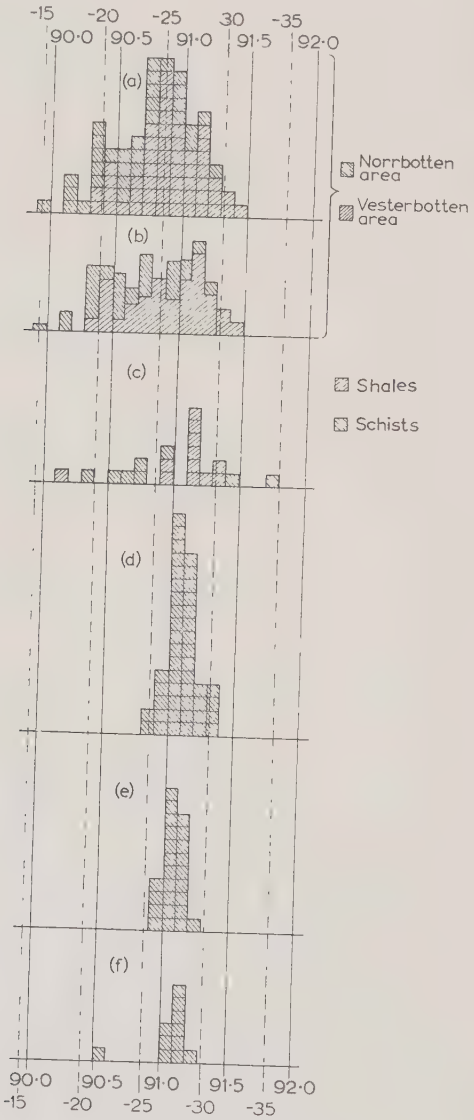

Fig. 2.

certainly not a quite satisfactory method either, and in order to present the entire results, both kinds of diagrams have been reproduced. However, the diagrams based on "unit locality" give the most correct survey of the qualitative distribution of values over the whole area examined.

Graphite from Pre-Cambrian slates, schists, and gneisses

Figs. 2(a) and 2(b) demonstrate the variations in the $^{12}C/^{13}C$-ratio in all graphitic samples from the Pre-Cambrian area under discussion. In Figs. 3 (c), (d), (e), and (f) some analyses from previous publications are presented, the results of which by calibration of the individual standards can be directly compared with the values obtained in the present investigation. They were chosen to represent rocks assumed to have an origin similar to those here analysed. A considerable number of analyses lie within the range of variation of the Cambro-Ordovician alum shales as deduced by LANDERGREN (1954) (Fig. 2(d), (e), and (f)). The diagram in Fig. 2(d) (LANDERGREN, 1954, Table 7) represents both vertical and lateral variations, Fig. 2(e) (LANDERGREN, 1954, Table 8) represents merely vertical variations, and Fig. 2(f) (LANDERGREN, 1954, Table 9) represents various stratigraphic zones from different localities. It will be observed that agreement between the three diagrams is mostly very good. The diagrams in Figs. 2(d) and 2(e) are founded on analyses of samples from drill holes. The following survey demonstrates the range of variation in each drill hole and consequently at the same "locality."

Locality (according to LANDERGREN, Tables 7 and 8	Number of analyses	Section in drill hole, covered by analyses	Range of variation of $^{12}C/^{13}C$
Motala	4	3·80 m	0·27
Skärlöf	3	1·70 m	0·08
Gislövshammar	5	3·00 m	0·12
Andrarum	10	4·92 m	0·18
Södra Sandby	45	88·02 m	0·53

In the following groups of analyses of graphite from Pre-Cambrian areas in northern Sweden (cf. Table 1), each group was computed so as to represent one locality for the diagram in Fig. 2(b):

	Range of variation of the ratio $^{12}C/^{13}C$
Nos. 19–26, Drill hole "Strömfors 3"	0·32
Nos. 32–37, Drill hole "Rutselheden 4"	0·05
Nos. 50–56, Drill hole "Rävliden 1"	0·24
Nos. 119–122, Drill hole "Meraslinka 2"	0·25

In the above four groups of analyses the various samples are exactly defined.

The following pairs of analyses are of samples from the same locality, the relative positions of which are not, however, known in detail:

		Difference in the ratio $^{12}C/^{13}C$
Nos. 40–41 "Skäggträskberget"	Vesterbotten	0·07
Nos. 94–95 "Armasvaara"	Norrbotten	0·10
Nos. 98–99 "Ristimela"	Norrbotten	0·03
Nos. 100–101 "Huuki"	Norrbotten	0·20
Nos. 126–127 "Aijärova"	Norrbotten	0·31
Nos. 129–130 "Svappavaara"	Norrbotten	0·15
Nos. 136–137 "Läppäkoski"	Norrbotten	1·07

With the one exception of Läppäkoski, the variations in the isotopic values at the various Pre-Cambrian localities do not display any exceptional features as compared with the variations at the localities of the Cambrio-Ordovician shales. The dispersion of values within the whole material is considerably higher, however, but is on the other hand of the same order of magnitude as in the shales from various geological systems and various parts of the world as presented by Craig (1953) (Fig. 2c). Since the Pre-Cambrian sediments of the present investigation have been affected by several kinds of transformations subsequent to their original deposition, the role of the post-depositional changes for a possible fractionation of the isotopes must of course be considered.

Some analyses presented by Wickman (1953) and Landergren (1955) have shown that pure thermal metamorphism of organic carbon in sediments as caused by magmas does not bring about any significant fractionation of the isotopes. Now, regional metamorphism of a rock mass includes many kinds of transformations (thermal metamorphism, kineto-metamorphism, metasomatism in connection with transfer of fluids and gases, reactions in the solid state, etc.). Craig (1953, p. 85) has emphasized that fractionation of isotopes at the formation of graphite must be dependent on the possible interaction of gases such as CO, CO_2, CH_4, H_2O, and H_2 and on the temperatures and rates of transformation. Since it is practically impossible to make any statement concerning the role of these factors during the metamorphism in the present case, the mere testimony of the analyses will be discussed with reference to metamorphism as indicated by mineralogical and structural features of the rocks.

The Vesterbotten area is best suited for an examination of the relations between grade of regional metamorphism and the variations in the isotope ratios. As was mentioned in the survey of the geological features (p. 298), a continuous change of progressive metamorphism can be established on the basis of certain index minerals and degree of recrystallization and mobilization. Fig. 3 is a survey of the relation between metamorphism in this sense and isotope ratio of graphite in schists and gneisses. The analyses are grouped according to the regional characteristics of

certain main areas: The Skellefte district proper with both volcanites and graphite-bearing slates and schists, the wide granite areas with large belts of graphite-schists, and the gneiss areas with subordinate granite. The localities of the Skellefte district are arranged roughly from west to east, in order to demonstrate

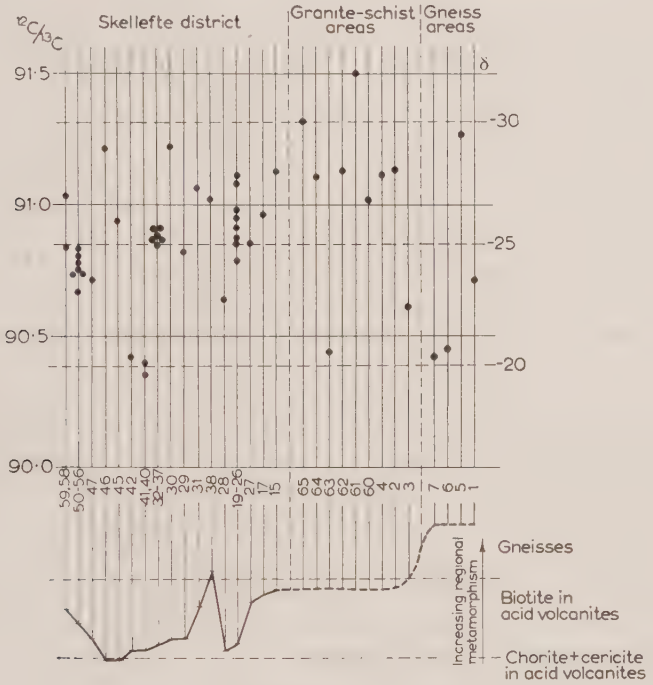

Fig. 3.

lateral distribution of the values within the district. From this survey it is impossible to discern any correlation between the variations in the isotope ratios and the grade of regional metamorphism.

If the individual groups of analyses are considered separately, there is nothing to indicate that the isotope ratios are related to variations in the grade of metamorphism. The locality at Läppäkoski is worth consideration, since there one of the high Norrbotten quotients is combined with the most exceptionally low quotient of the entire material. Megascopically, the two samples are very similar, but the low-quotient sample contains blebs of quartz, lime-silicates, and sulphides. If the low $^{12}C/^{13}C$ value in this case was caused, for example, by some kind of reduction of carbonate carbon in connection with the introduction of sulphides, this must be an exceptional case, for in other groups no correlation between content of sulphides and the isotopic ratios could be observed.

The amount of graphite carbon in the samples analysed may vary between less than 1 per cent and almost pure graphite masses. These divergencies may of course be due to differences in the carbon content in the original sediment as well as to a secondary concentration of carbonaceous material. An attempt to correlate

the percentages of carbon in the sediments with the isotope quotients was without success.

If the three main rock units as presented in Fig. 3 are compared, the Skellefte district is found to be characterized by a prevalence of intermediate values of the $^{12}C/^{13}C$ ratio, the granite-schist areas by a prevalence of high values, and the gneisses possibly by a prevalence of low values, but in each of these three groups both high and low values do occur. Are the divergencies mentioned significant of some kind of post-depositional change or do they reflect different isotopic fractionation during the formation of the bituminous sediments? It can be assumed that within the gneissose areas a more thorough interaction of solutions and gases has occurred at metamorphism than in the granite-schist areas and in the Skellefte district proper. With respect to the role that might be assigned to a fluid or gaseous phase at the formation of graphite, this could be taken to explain the low $^{12}C/^{13}C$ values in the gneisses. On the other hand, there is nothing to indicate that the low quotients of the Skellefte district (Nos. 40, 41, 59) have a similar cause. It seems much more likely that these values represent the approximate isotopic composition of the original carbonaceous sediment.

Since analyses of the isotopic composition of carbon from low-metamorphic shales (Fig. 2c) show that the isotopic fractionation may vary from case to case, probably owing to local conditions, the role of varying sedimentogenic environments must also be considered in an attempt to explain the variations of the isotope ratio as found in the present investigation. Unfortunately, the post-depositional changes in the material examined, the scattered and irregular distribution of outcrops, and the complicated tectonic pattern make it almost impossible to obtain a satisfactory idea of conditions at the accumulation and sedimentation of the carbonaceous material. Some more regional features can be stated, however: In the Skellefte district the graphitic sediments form fairly thin beds associated with volcanites or represent the lowest portions of the large mass of sediments extending southwards from the Skellefte district. The samples from the gneissose areas and the areas of granites and schists come from the interior of this vast area of sediments, and they may have any stratigraphic position in the wide sedimentary sequence. Nothing definite can be stated concerning any general difference of the sedimentogenic conditions between the gneissose areas and the granite–schist areas. The only argument that can be presented in favour of a possible difference in sedimentogenic environment is the fact that they represent two spatially separate rock units, and therefore the sediments may have originated under somewhat different conditions.

Different conditions of sedimentation as indicated by variations in the lithological development of the sediments within a restricted area has been without influence on the isotopic ratio. This is shown by the analyses from the drill holes "Rutselheden 4," (nos. 32–37), "Strömfors 3." (nos. 19–26), and "Rävliden 1," (nos. 50–56). In the first two drill holes of this group, the entire section covered by analyses is very homogeneous and the various samples are, megascopically, practically identical. The series of analyses from "Rävliden 1" covers a much wider section of the sedimentary sequence. The sediments within this section are highly variable—beds of various thickness of graphitic black slate, grey slate,

sandstone, and greywacke, sometimes conglomeratic, alternate irregularly. The analyses from "Rävliden 1" thus represent variations in the isotopic ratio formed under swiftly changing conditions of sedimentation. The range of variation is by no means exceptional, however, and even lower than in the group from the drill hole "Strömfors No. 3."

The $^{12}C/^{13}C$ ratio in metamorphic bituminous sediments from the Caledonian mountains of Sweden

In order to elucidate the variations in the $^{12}C/^{13}C$ ratio of carbon from metamorphic areas by additional analyses, twenty-five samples of metamorphic Cambro-Silurian graphite argillites from the Caledonian mountain range were examined. The Cambro-Silurian rocks of the Scandinavian Caledonian mountains are divided into two main groups representing two different sedimentogenic facies, the eastern and the western Cambro-Silurian facies. The sediments of the eastern facies were deposited on the eastern border of the Caledonian geosyncline and are closely related to the unfolded Cambro-Silurian sediments occurring east of the Caledonian belt. The Cambro-Ordovician sediments examined by Landergren come from these unfolded areas.

Tectonically, the eastern Cambro-Silurian facies along the border of the Caledonian belt is autochtonous or para-autochtonous. Several thrust sheets exist in the centre of the Caledonides, the lowest containing sediments of typical eastern facies, the upper sheets, however, also with sediments which are more a greywacke facies (Asklund, 1946, p. 238). Towards the west all these rocks are separated by a great thrust plane from one or several thrusts sheets; these are built up of typical geosynclinal sediments—the western Cambro-Silurian facies—which consequently forms the uppermost part of the thrust masses. Regional metamorphism varies from a low-grade green-schist facies to an amphibolite facies or gneissose rocks.

Bituminous sediments occur in both the sediments of the eastern and western facies. Their content of carbonate is generally low and does not, at least, exceed the carbonate content of the normal alum shales. Since bituminous shales have a very low folding competence, they are apt to be very strongly sheared by stress. The $^{12}C/^{13}C$ ratios for twenty-five samples from the metamorphic forms of originally bituminous shales have been determined, the results being summarized in Fig. 4. Megascopically several of these samples do not differ from corresponding rocks in the Pre-Cambrian areas discussed previously in this paper. Seven samples represent the eastern Cambro-Silurian border facies, and two occur in the interior of the mountain belt, but are assumed to represent the same stratigraphical zone. The remaining sixteen samples represent the western Cambro-Silurian facies. Fig. 4 demonstrates that the eastern border facies and the western facies are characterized by two different groups with respect to isotope ratios. Actually they do not even overlap, since the range of variation in the $^{12}C/^{13}C$ ratio is 90·99–91·17 and 90·39–90·96 respectively. The eight values denoted by "*s*" in Fig. 4 are from one drill hole (covering a section of 22·80 m) and thus indicate the variations at one "locality." The range of variation within this group is 90·45–90·85, which is not much lower than in the group where the samples are from various localities scattered over a wide area.

The rocks of the eastern border facies and the western facies differ in three respects, viz. conditions of accumulation and deposition of the sediments, tectonic evolution, and structural position in the mountain range and degree of metamorphism. The samples analysed have been chosen to denote various degrees of kineto-metamorphism; some of them come from the thrust zones and are intensely

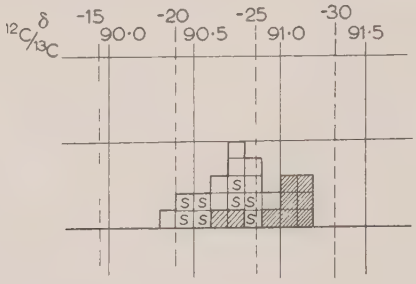

Fig. 4.

mylonitized, others derive from the interior of the thrust masses or from the para-autochtonous sediments. All the samples are fairly intensely sheared, however, and megascopically they do not differ very much. If the variations in the $^{12}C/^{13}C$ ratios in the sixteen samples from the western facies rocks are considered, no correlation between intensity of kineto-metamorphism and isotopic composition of the graphites can be noted. Since the variations within the drill-hole section (22·8 m) are of the same order of magnitude as in the other material and since no important thrust plane is known to occur within the section penetrated by the drill hole, it is seen that the $^{12}C/^{13}C$ ratio does vary, irrespective of the variations in kineto-morphism. Neither is there anything in this material to indicate that regional metamorphism significantly influenced the isotopic composition.

Fig. 4 demonstrates that the group of $^{12}C/^{13}C$ values representing sediments of the eastern border facies is in full agreement with the values found by Landergren to be characteristic of the Cambro-Ordovician alum shales outside the Caledonian belt. Since all geological and palaeontological evidence indicates similar sedimentogenic evolution in the two environments mentioned, it is reasonable to assume that the agreement with respect to isotopic composition between the two areas mentioned is due to the similar sedimentogenic conditions, and further, that the kineto-metamorphism which was active in the eastern Caledonian border zone did not notably influence the isotopic composition.

The samples indicative of the western Caledonian facies have $^{12}C/^{13}C$ values which were found to be very common among the Pre-Cambrain areas examined. As was mentioned above, the sediments of the western facies originated under conditions quite different from those prevailing in and east of the Caledonian border area. In a survey of analyses of various Scandinavian sediments of Cambro-Silurian age, Kulling (1933) demonstrated that the bituminous argillaceous sediments of the western facies differ also in chemical respect from the alum shales:

they are richer in magnesium and sodium, and poorer in potassium. On the whole, they can be considered to represent accumulations of more poorly sorted detritus, which is in accordance with their appearance in a geosyncline facies.

The two values denoting the same stratigraphical position as the eastern facies sediments but occurring within the inner part of the Caledonian belt coincide with the values of the western facies sediments. These two analysed samples are somewhat more arenaceous than most of the other eastern facies argillites, but there is otherwise very little in the lithological development of the sediments under consideration that indicates a sedimentation much different from that of the other rocks of the eastern border facies. Their location closer to the growing geosyncline in the west and their slightly arenaceous development may, however, be indicative of conditions of formation somewhat different from those prevailing during the deposition of the normal alum shales.

The above thus agrees with the considerations concerning the Pre-Cambrian area. It seems plausible that the variations in the isotope values were, at least to a great extent, developed in connection with the origin of the sediments and were dependent on specific sedimentogenic conditions. In this connection it is worth remembering that the graphitic sediments in the Pre-Cambrian areas occur in a sequence of sediments that, according to Pettijohn's classification (1949), represent the "greywacke series" and therefore are, broadly speaking, more closely related to the western than to the eastern Caledonian facies.

Summary and Conclusions

The Pre-Cambrian graphitic sediments examined show the same range of variation in the $^{12}C/^{13}C$ ratio as has been given in previous papers. The absence of a well-defined maximum in the diagrams of the entire material presented in Fig. 2(a) and (b) could be taken as an indication of post-depositional fractionation in connection with metamorphism, but consideration of the variations in detail lends little support to this interpretation. No correlation can be discerned between isotopic composition on the one hand and grade of regional metamorphism (as indicated by mineralogical and structural features) or pure kineto-metamorphism of originally bituminous sediments on the other.

If the isotope ratios within restricted portions of the sedimentary sequences are considered separately, the ranges of variations are in most cases by no means exceptional as compared with corresponding portions of sediments from younger geological systems, discussions of which have appeared in previous papers. There are actually some indications that the divergences in isotopic composition between certain groups of values are dependent on the original conditions prevailing during the accumulation of carbonaceous matter. This last interpretation certainly needs confirmation by additional investigations from areas where rock evolution can be demonstrated with a higher degree of accuracy, but if it holds true, it would be a very valuable contribution for many kinds of petrogenetical work, particularly in Pre-Cambrian areas.

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Semi-quantitative spectrographic analysis and rank correlation in geochemistry*

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Abstract—The rank correlation coefficient, r_s, which involves less computation than the product-moment correlation coefficient, r, can be used to indicate the degree of relationship between two elements. The method is applicable in situations where the assumptions underlying normal distribution correlation theory may not be satisfied. Semi-quantitative spectrographic analyses which are reported as grouped or partly ranked data can be used to calculate rank correlations between elements.

Introduction

One of the major problems in geochemistry is the origin of ore deposits. An approach to the solution of this problem is the study of the relationship between elements in and around deposits.

The relation between such elements is usually measured by the product-moment correlation coefficient, r, and the significance or non-significance of the association is obtained by reference to tables of correlation coefficients at the 1 per cent and 5 per cent levels of significance (Snedecor, 1946; Fisher and Yates, 1948) for different degrees of freedom. In practice, normality of the parent populations, independence of successive pairs of observations, and homogeneity of variances are generally, and very frequently unknowingly, assumed. However, because of its value to workers in the geological sciences, this use of the method should not be rejected in spite of both the tediousness of computations where a large number of pairs of observations are involved and the failure to validate the assumptions.

Rank Correlation

The calculation of correlation coefficients by the method of least-squares is tedious when the data consist of two variables each with three significant figures, and when there are twenty or more pairs of such variables. Such a situation is common in geochemical work where many chemical analyses are reported to three significant figures.

Both computational labour and verification of the basic assumptions can be avoided by calculating Spearman's rank correlation coefficient. The method is non-parametric and the assumptions need not be made. Like the product-moment correlation coefficient, the rank correlation coefficient, r_s, can assume values between ± 1, with larger absolute values indicating a higher degree of association. However, values of r_s should not be compared with those of r, even though they usually agree in sign and very roughly in order of magnitude, as r_s is not appropriately interpreted as an estimator of the population product moment correlation, ρ, even when normal theory assumptions hold.

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Computations are rapid, and if the results are not sufficiently precise for the purpose at hand—for example, a general search for associations—they can be used to determine priorities for the more involved calculations of the usual correlation coefficient. The theoretical aspects of the method have been treated by Kendall (1948), and many texts, including one with chemical examples (Bennett and Franklin, 1954), give the algebraic derivation of the expression used to calculate the rank correlation coefficient.

The method of computation is briefly as follows: in a set of n samples on which elements x and y have both been determined, the determinations of element x can be arranged in increasing numerical value and ranked from 1, 2, 3, . . ., to n, where rank 1 contains the least and rank n the greatest amount of element x. The y observations are similarly ranked. The difference between the ranks for x and y is taken for each sample, squared, and these squared rank differences $[(R.D.)^2]$ summed over the n samples. The Spearman rank correlation coefficient r_s can then be calculated from

$$r_s = 1 - \frac{6\Sigma(R.D.)^2}{n(n^2 - 1)} \tag{1}$$

The null hypothesis that there is no association or that all permutations of one ranking relative to the other are equally likely, is then set up and the significance of r_s tested by

$$t_{n-2} = r_s\sqrt{\{(n - 2)/(1 - r_s^2)\}} \tag{2}$$

as Student's "t" is a good approximation to the distribution of the function of r above for $n \geqslant 9$ (Kendall, 1948, pp. 46–47). It might also be noted that for larger-size samples ($n > 20$) the normal distribution is a good approximation to the distribution of $r_s\sqrt{(n - 1)}$.

If, however, one substitutes for r_s in (2), the resulting expression can be rearranged to give

$$\Sigma(R.D.)^2 = \frac{n^3 - n}{6}\left[1 \pm \sqrt{\left(\frac{t^2}{n - 2 + t^2}\right)}\right] \tag{3}$$

Substitution of t with $n - 2$ degrees of freedom into this last equation allows calculations of upper and lower limits for the sum of the squared rank differences. The exact distribution of the sum of the squared rank differences has been studied by Kendall (1948), and Olds (1938, 1949) has tabulated these sums for n from 5 to 30. Litchfield and Wilcoxon (1955) have recently extended these tables from $n = 31$ to $n = 40$ (Table 1) and in addition have prepared a nomograph (Fig. 1) from which, knowing n and $\Sigma(R.D.)^2$, the rank correlation coefficient, r_s, can be read directly.

Semi-quantitative Spectrographic Analyses in Rank Correlation

The spectrograph has been shown by Waring and Annell (1953) to be a useful tool for the semi-quantitative determination of sixty-eight elements. The results of the analysis were reported in brackets of powers of ten, i.e. 0·01–0·1, 0·1–1·0, 1·0–10·0, and the authors estimated about 90 per cent agreement with chemical results. The method has been modified, and the spectrographic laboratories

Table 1. Critical values of $\Sigma(R.D.)^2$

n*	Probability 0·05	0·01	n*	Probability 0·05	0·01
			21	873–2207	695–2385
			22	1022–2520	820–2722
			23	1187–2861	960–3088
			24	1370–3230	1115–3485
5	0–40		25	1570–3630	1287–3913
6	4–66	0–70	26	1789–4061	1475–4375
7	12–100	4–108	27	2028–4524	1681–4871
8	22–146	10–158	28	2287–5021	1906–5402
9	40–200	24–216	29	2569–5551	2149–5971
10	61–269	39–291	30	2873–6117	2414–6576
11	88–352	58–382	31	3199–6721	2700–7220
12	121–451	84–488	32	3550–7362	3008–7904
13	163–565	115–613	33	3926–8042	3338–8630
14	213–697	154–756	34	4328–8762	3693–9397
15	272–848	201–919	35	4757–9523	4073–10,207
16	342–1018	257–1103	36	5213–10,327	4476–11,064
17	423–1209	322–1310	37	5698–11,174	4908–11,964
18	515–1423	398–1540	38	6213–12,065	5366–12,912
19	621–1659	484–1796	39	6758–13,002	5853–13,907
20	740–1920	583–2077	40	7334–13,986	6367–14,953

* n = number of pairs ranked.

Use of table: If the observed total is equal to or less than the appropriate lower tabular value, or equal to or greater than the appropriate higher tabular value, the correlation is significant for that probability. High values correspond to negative correlations, and low values to positive correlations.

of the U.S. Geological Survey now report semi-quantitative determinations in two brackets per power of ten, although in some special cases determinations were reported in three brackets per power of ten. The first of these divides the samples into brackets of 0·1–0·5 and 0·5–1·0 for powers of ten, and 80 per cent agreement is estimated. The three-bracket system is based on intervals of $1–\sqrt[3]{10}$, $\sqrt[3]{10}–\sqrt[3]{10^2}$, and $\sqrt[3]{10^2}–\sqrt[3]{10^3}$ for any power of 10, and these can be represented numerically with no significance attached to the digits as 1·2·1, 2·1–4·6, and 4·6·10. Sixty per cent agreement is estimated for this three-bracket reporting system.

The one-, two-, and three-bracket systems of reporting have the common property that they almost automatically rank the determinations. This is more obvious in the one-bracket system, where, if there were one each of four determinations reported in the four brackets 0·001–0·01, 0·01–0·1, 0·1–1, and 1–10, it can be seen that the powers of ten of the lower bound of each bracket are −3, −2, −1, and zero, respectively. By adding a digit to the exponent of the lower bound of the lowest bracket so that the addition results in +1 for this bracket, correct ranks are automatically assigned. Hence, by adding 4 to the exponents above, the ranks of 1, 2, 3, and 4 are obtained respectively. This is an excellent procedure where there is one observation per bracket.

This simple procedure is not directly applicable to the two- or three-bracket

systems nor to the one-bracket system where three are no entries in an intermediate bracket, or where there are replicate entries in one or more brackets. In these cases the brackets must be arranged in increasing numerical value and the observations ranked in the usual fashion.

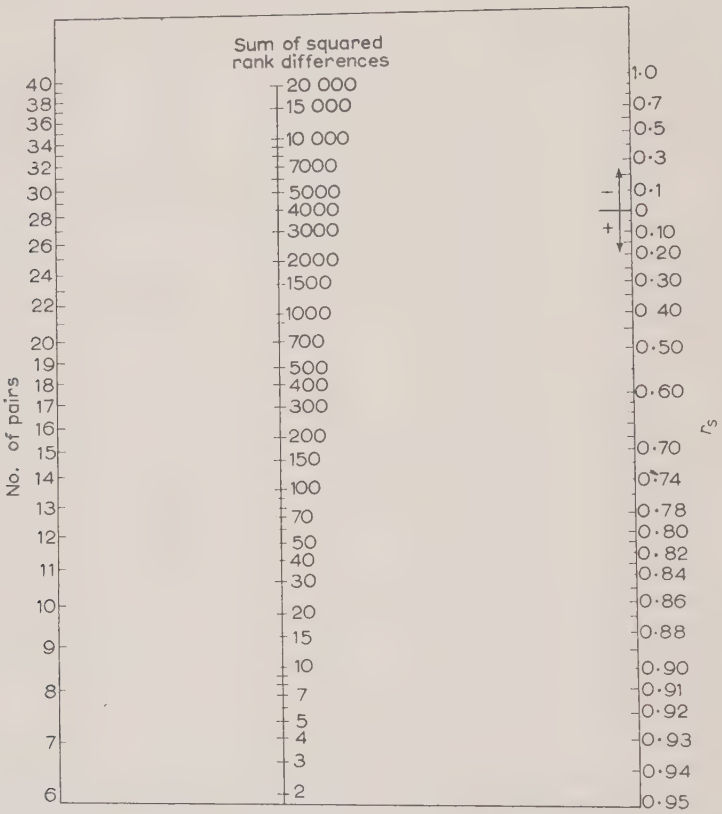

Fig. 1. Nomograph for r_s, the rank correlation coefficient (Litchfield and Wilcoxon, 1955).

As these methods of reporting semi-quantitative data partly rank the observations and the ranking itself is easily accomplished, the merits of using this kind of data for the calculation of rank correlation coefficients are obvious. One disadvantage of using semi-quantitative spectrographic data is that the data are grouped and hence tied ranks occur.

As an example, a set of ten observations of this kind might be distributed 1, 3, 4, and 2 in four brackets. As the measurement process does not distinguish among members of the group, ties are assigned the mean value of the ranks. The observation in the first bracket is ranked 1. In the second bracket the ranks would have been 2, 3, and 4 had the observations been slightly different. The mean of these three ranks is 3, and hence the observations in the second bracket are ranked 3, 3, and 3. The mean rank of the next bracket is 6·5, or $(5 + 6 + 7 + 8)/4$, and the four observations are each ranked 6·5. In a similar fashion the last two observations are each ranked 9·5. The rank correlation coefficient is affected by

ties, and corrections can be applied (KENDALL, 1948; SIEGEL, 1956). As the presence of tied ranks has been ignored in both Table 1 and in the nomograph, it should be noted that the use of Table 1 provides only an approximate test of significance and that values of r_s estimated from the nomograph are approximate.

The applicability of semi-quantitative spectrographic analyses to rank correlation can be seen in Table 2, which contains data for samples collected by A. F. TRITES JR., U.S. Geological Survey. The data consist of chemical and semi-quantitative analyses of copper, and manganese. The spectrographic data are reported in the three-bracket system.

Many geologic investigations require both chemical and semi-quantitative spectrographic analyses for the same group of samples. If the investigator is interested in the degree of association between two elements which have been determined chemically, he can usually calculate the product-moment correlation coefficient. If either or both the percentages of the pair of elements have been expressed as semi-quantitative spectrographic data that are ranked data, the product-moment coefficient cannot be calculated and the usual result is a rough visual comparison made between pairs. However, it is possible, where one or both sets of data are semi-quantitative, to rank both sets of data and to estimate the degree of association by the rank correlation coefficient, r_s. An example of a calculation of the sum of squared rank differences, $\Sigma(R.D.)^2$, using the mixed type of data, is shown in Table 3.

As the method is applicable to continuous data (chemical analyses, for example) and to ranked data (semi-quantitative spectrographic analyses), or to mixtures of both, it is of interest to calculate all possible correlation coefficients. Assuming that the basic assumptions associated with correlation have been validated, the product-moment correlation coefficient, using the chemical data, can be calculated. The four sets of data have been ranked as shown in Table 2 and r_s calculated for the following ranked pairs, Cu_c–Mn_c, Cu_c–Mn_s, Cu_s–Mn_s, and Cu_s–Mn_c, where subscripts c and s refer to chemical and spectrographic data.

If in the original spectrographic data, transformations of the type $0{\cdot}0\,Z^{\mp} = 0{\cdot}0X^{+}$ and $0{\cdot}0Z = 0{\cdot}0X^{-} + 0{\cdot}0X$ are made, the three-bracket data can be changed to the two-bracket system of reporting and hence the original data used to illustrate ranks obtained from two-bracket data. In making use of this transformation. the assumptions have been made that (1) there is equal accuracy of placing values in the correct brackets, (2) the lower bracket of the two-bracket system is identical to the lower two of the three-bracket system, and (3) the results of the transformation represent actual readings by a spectrographer. Having made the transformations, the spectrographic data for the two elements can be ranked as shown in Table 2 and r_s calculated for them as well as for the pairs, Cu_c–Mn_s and Cu_s–Mn_c. The sums of squared rank differences and the calculated rank correlation coefficients are shown for each pair in Table 4.

Table 4 shows that only one sum of squared rank differences (516) lies inside the region (515–1423) in which the correlation is not significant at the 0·05 level. However, this should not cause too much concern as the value is just inside the limit. It can be postulated that the transformations made, plus the non-validated assumptions, have affected the rank correlation coefficients as can be noted by

Table 2. Ranks of chemical and spectrographic determinations of copper and manganese*

Copper					Manganese				
Electrolytic		Spectrographic			Chemical		Spectrographic		
Per cent	Rank	Range (per cent) (3-bracket)†	Rank 3-bracket	Rank 2-bracket	Per cent	Rank	Range (per cent) (3-bracket)†	Rank 3-bracket	Rank 2-bracket
0·03	3·5	0·0X	3	3	0·014	2	0·0X^-	3	6·5
0·028	2	0·0X	3	3	0·029	5·5	0·00X	1·5	1·5
0·24	12	0·X	10·5	9·5	0·064	10	0·0X	7	6·5
0·16	9·5	0·X	10·5	9·5	0·021	3	0·0X	7	6·5
1·81	16	X·	17	17	0·174	17	0·X	17·5	15
0·15	8	0·X	10·5	9·5	0·106	15	0·X^-	14	15
0·74	14	0·X^+	14·5	14·5	0·095	14	0·X^-	14	15
0·10	6	0·X^-	6·5	9·5	0·022	4	0·0X	7	6·5
2·06	17	X·	17	17	0·041	7	0·0X	7	6·5
1·0	15	0·X^+	14·5	14·5	0·052	9	0·0X	7	6·5
3·3	18	X·	17	17	0·206	18	0·X	17·5	15
0·023	1	0·0X	3	3	0·029	5·5	0·0X	7	6·5
0·09	5	0·0X	3	3	0·094	13	0·X^-	14	15
0·03	3·5	0·0X	3	3	0·007	1	0·00X	1·5	1·5
0·22	11	0·X	10·5	9·5	0·048	8	0·0X	7	6·5
0·16	9·5	0·X^-	6·5	9·5	0·077	11	0·0X^+	11	11
0·41	13	0·X	10·5	9·5	0·130	16	0·X^-	14	15
0·14	7	0·X	10·5	9·5	0·087	12	0·X^-	14	15

* Samples collected by A. F. Trites Jr. Copper determinations by A. C. Horr and D. L. Skinner; manganese determinations by J. F. Wahlberg; and spectrographic determinations by R. C. Havens, all members of the U.S. Geological Survey.

† Ranges X^-, X, and X^+ for any power of 10 correspond to intervals $1-\sqrt[3]{10}$, $\sqrt[3]{10}$ $\sqrt[3]{10^2}$, and $\sqrt[3]{10^2}-\sqrt[3]{10^3}$ respectively.

Table 3. Calculation of the sum of squared rank differences

Copper		Manganese		$R.D.$* (Cu − Mn)	$(R.D.)^2$
Per cent	Rank	Range (3-bracket)	Rank		
0·03	3·5	$0{\cdot}0X^-$	3	0·5	0·25
0·028	2	$0{\cdot}00X$	1·5	0·5	·25
0·24	12	$0{\cdot}0X$	7	5	25·
0·16	9·5	$0{\cdot}0X$	7	2·5	6·25
1·81	16	$0{\cdot}X$	17·5	−1.5	2·25
0·15	8	$0{\cdot}X^-$	14	−6	36·
0·74	14	$0{\cdot}X^-$	14	0	0
0·10	6	$0{\cdot}0X$	7	−1	1
2·06	17	$0{\cdot}0X$	7	10	100
1·0	15	$0{\cdot}0X$	7	8	64
3·3	18	$0{\cdot}X$	17·5	0·5	·25
0·023	1	$0{\cdot}0X$	7	−6	36
0·09	5	$0{\cdot}X^-$	14	−9	81
0·03	3·5	$0{\cdot}00X$	1·5	2	4
0·22	11	$0{\cdot}0X$	7	4	16
0·16	9·5	$0{\cdot}0X^+$	11	−1·5	2·25
0·41	13	$0{\cdot}X^-$	14	−1	1
0·14	7	$0{\cdot}X^-$	14	−7	49
				$\Sigma(R.D.)^2 = 424{\cdot}50$	

* Rank differences

Table 4. $\Sigma(R.D.)^2$ and r_s

Pair of ranked variables	$\Sigma(R.D.)^2$	r_s
Cu_c–Mn_c	386·5	0·60
Cu_s–Mn_s (3-bracket)	392·5	0·60
Cu_c–Mn_s (3-bracket)	424·5	0·56
Cu_s–Mn_c (3-bracket)	391·0	0·60
Cu_s–Mn_s (2-bracket)	484·5	0·50
Cu_c–Mn_s (2-bracket)	516·0*	0·47
Cu_s–Mn_c (2-bracket)	405·0	0·58
Product moment correlation coefficient for Cu_c–Mn_c = 0·66		

* Correlation is not significant.

comparing the values for three-bracket results with those for two-bracket determinations.

Inspection of the coefficients in Table 4 shows that all ranked pairs of types of data furnish estimates that agree fairly closely within themselves. Hence, semi-quantitative spectrographic data, which are cruder measurements than chemical data, can be used to obtain estimates of the degree of association by rank correlation.

Although it is not appropriate to compare r and r_s, the data in Table 4 show that they agree in sign and roughly in order of magnitude.

Although the simplicity of calculation is destroyed where the adjustment for tied ranks is introduced (Kendall, 1948), the adjustment should be made where the data contain a large number of tied groups (Siegel, 1956) and where the significance of the association is of marginal value. The unadjusted and the adjusted coefficients are shown in Table 5. These coefficients show that the adjustment does not always have the effect of lowering the numerical value of r_s.

Table 5. Rank correlation coefficients adjusted for ties

Pair of ranked variables	r_s (unadjusted)	r_s (adjusted)
Cu_c–Mn_c	0·60	0·60
Cu_s–Mn_s (3-bracket)	0·60	0·56
Cu_c–Mn_s (3-bracket)	0·56	0·54
Cu_s–Mn_c (3-bracket)	0·60	0·58
Cu_s–Mn_s (2-bracket)	0·50	0·43
Cu_c–Mn_s (2-bracket)	0·47	0·43
Cu_s–Mn_c (2-bracket)	0·58	0·56

For rough estimates of the degree of association between pairs of elements in a group of samples, Spearman's rank correlation is recommended because of computational ease. However, the adjustment for ties should be made where a large number occur and where the significance of the sum of the squared rank differences or of the coefficient r_s tends to be marginal.

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Argonbestimmungen an Kaliummineralien—IV

Die Frage der Argonverluste in Kalifeldspäten und Glimmermineralien

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Abstract—The age of different samples of felspar and mica were determined by the potassium-argon method.

It was shown that the argon content of felspar is about 5 per cent less than the content of mica in the pegmatite from Hechtsberg, Black Forest, Germany (age *c.* 250 million years). Approximately the same result was found with the pegmatite from Hobol, South Norway (age *c.* 960 million years). Careful analyses of those samples with a polarizing microscope showed the existence of metamorphic transformations in the felspar. This seems to be the reason for the loss of argon in felspar. In addition, some measurements were made of the argon losses in different grain sizes of felspar. Losses of argon were first observed when the felspar was pulverized to a grain size of less than 100 microns. On further pulverizing the felspar to a grain size of 5 to 10 microns, argon losses of 30 to 50 per cent were found.

In unseren früheren Arbeiten (Smits und Gentner, 1950; Gentner *et al.*, 1953; Gentner *et al.*, 1954a; 1954b; Gentner *et al.*, 1955) berichteten wir über Argonbestimmungen an Kalisalzen und Messungen des Heliumgehaltes von tertiären Sylvinen. Wir konnten damals feststellen, dass in den Sylvinen Argon- und Heliumverluste auftreten und konnten diese Verluste durch Messungen der Diffusionskonstanten von Argon und Helium in tertiären Sylvinen quantitativ erfassen. Für die zur Altersbestimmung wichtigsten Mineralien Feldspat und Glimmer konnte aber bis heute keine definitive Aussage gemacht werden, ob auch hier mit einer Argondiffusion zu rechnen ist. Um sich hierüber Gewissheit zu verschaffen, wurden von uns mehrere Messreihen durchgeführt: Einmal haben wir Altersbestimmungen an Feldspäten und Glimmer ausgeführt, die aus demselben Pegmatit stammen, also das gleiche Alter haben. Sollte sich hierbei ein Altersunterschied der Mineralien ergeben, so kann bereits entschieden werden, welches Mineral relativ grössere Argonverluste erleidet. Aus denselben Gründen wurden bei Feldspäten auch Argonbestimmungen in Abhängigkeit von der Korngrösse durchgeführt, um bei evtl. auftretenden Argonverlusten Schwankungen im Argongehalt festzustellen.

Die bei diesen Messungen verwendete Aufschluss- und Messtechnik wurde in den früheren Arbeiten (Smits und Genter, 1950; Gentner *et al.*, 1953; Gentner *et al.*, 1954a, 1954b; Gentner *et al.*, 1955) bereits beschrieben. Es sei an dieser Stelle hervorgehoben, dass alle Messungen massenspektrometrisch auf Luftargon untersucht und korrigiert wurden, da geringe Verunreinigungen durch Luftargon nicht zu verhindern sind.

Die Messungen an den Feldspäten und Glimmern aus den Pegmatiten wurden nur an ausgesuchtem und mikroskopisch geprüftem Material durchgeführt. Die Ergebnisse der Einzelmessungen haben wir in Tabelle 1 zusammengestellt. Die Fehlerangabe der Alterswerte bezieht sich nur auf die Messungenauigkeit von Argon- und Kaliumgehalt der einzelnen Proben, nicht aber auf einen Genauigkeitsanpruch des absoluten Alters. Für die Altersberechnung wurde das Verzweigungsverhältnis $\lambda\kappa : \lambda_\beta = 0{,}120$ verwendet.

Tabelle 1. Ergebnisse der Altersbestimmung an Feldspäten und Glimmern, die aus demselben Pegmatit stammen

	Material	Lfd. Nr.	% Kal.	mm^3 rad. ^{40}A / g Material	mm^3 rad. ^{40}A / g Kalium	Alter in $10^6 a$
Pegmatit Hechtsberg	Biotit	66	6,51	0,069	1,06	255 ± 5%
		67	5,59	0,059	1,059	254 ± 5%
	Feldspat	68	6,57	0,0662	1,005	243 ± 5%
		69	5,32	0,052	0.98	237 ± 5%
		70	1,16	0,0119	1.03	248,5 ± 5%
Pegmatit Hobol Hyttasen	Orthoklas	201		0,470		
		202	10,5	0,465	4,47	895 ± 5%
		107		0,48		
		504		0,469		
	Muskovit	509		0,433		
		510	8,8	0,428	4,89	965 ± 5%

Wie aus Tabelle 1 zu ersehen ist, erhalten wir folgende Mittelwerte:

Pegmatit Hechtsberg:	Biotit	$255 \cdot 10^6 a$ ± 5%
Schwarzwald	Feldspat	$243 \cdot 10^6 a$ ± 5%
Pegmatit Hobol:	Muskovit	$965 \cdot 10^6 a$ ± 5%
Südnorwegen	Orthoklas	$895 \cdot 10^6 a$ ± 5%

Dieses Ergebnis war etwas überraschend, da man bei der sehr guten Spaltbarkeit des monoklinen Glimmers viel eher Argonverluste erwarten würde, als bei den ebenfalls monoklinen bzw. triklinen Feldspäten. Die Erklärung für die unterschiedlichen Messergebnisse darf jedoch nicht bei der unterschiedlichen Spaltbarkeit gesucht werden, sondern in der verschiedenen Stabilität der einzelnen Minerale gegen metamorphe Umbildungen. Der Kalifeldspat ist bedeutend instabiler gegen metamorphe Umbildung als der Glimmer. Bei den Kalifeldspäten treten hauptsächlich die Kaolinisierung und Serizitisierung als metamorphe Umbildung auf. Es wird dabei Kalifeldspat in Kaolin bzw. Muskovit umgebildet. Diese Metamorphosen sind den Kristallen äusserlich nicht anzusehen, zumal sie bei hydrothermalen Verhältnissen im Innern aller Feldspatkristalle auftreten. Beide metamorphe Umbildungsarten haben Argonverluste zur Folge, wenn sie auch nur sehr kleine Bereiche von der Grössenordnung μ im Kristall erfassen. Dünnschliffe von den Feldspäten zeigten auch Spuren der Kaolinisierung und Serizitschuppen von 5 μ. Im Polarisationsmikroskop ergab sich etwa folgendes Bild von den Kalifeldspäten: (Abb. 1).

Die Grösse dieser metamorph umgebildeten Bereiche bewegte sich zwischen 1–5 μ bzw. 5–30 μ, während die Abstände dieser Gebiete 5–50 μ betragen.

Ein weiterer Nachteil der Kalifeldspäte ist der, dass sie bei der Kristallisation mit Natriumfeldspat Mischkristalle bilden (die Kalifeldspäte enthalten 2–3% Natrium), die sich bei tiefen Temperaturen (300–500°C) wieder entmischen können,

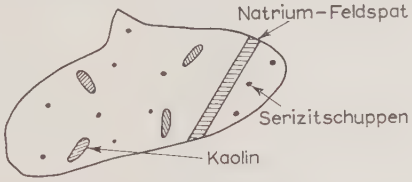

Abb. 1. Bild eines Kalifeldspatdünnschliffes im Polarisationsmikroskop.

was zu der bekannten Lamellenbildung der Kali-Natronfeldspäte führt, die sehr leicht im Polarisationsmikroskop zu erkennen ist. In den untersuchten Proben fanden wir Lamellen von Natriumfeldspat mit einer Breite von 5–30 μ. Die Entsmischungslamellen können jedoch auch submikroskopische Werte annehmen. Neben der metamorphen Umbildung verursachen deshalb auch die Entmischung der Kristalle innere Oberflächen und Korngrenzen. Neben der metamorphen Umbildung wird deshalb auch die Entmischung der Mischkristalle weitgehend für den Altersunterschied von Glimmer und Feldspat verantwortlich sein, da beide Vorgänge in den Feldspäten Argonverluste zur Folge haben.

Neben den oben diskutierten Argonverlusten kann aber bei den Kalifeldspäten noch eine echte Volumendiffusion erfolgen. Da die Kalifeldspäte zu den Gerüstsilikaten gehören, ist bei ihnen eine isotrope Diffusion möglich, während bei der Struktur des Glimmers nur eine Diffusion in den Netzebenen erfolgen kann. In Richtung der z-Achse ist bei den Glimmern keine Argondiffusion möglich, da die dichte Packung der SiO_4 Tetraeder keine Argonatome durchtreten lassen. Tritt nun bei den Kalifeldspäten noch eine echte Volumendiffusion hinzu, so müsste sich aber das diffundierende Argon an den durch Metamorphose und Lamellenbildung entstandenen Korngrenzen und inneren Oberflächen ansammeln, sofern es nicht den Kristallverband verlassen kann. Hier besteht nun die Möglichkeit, den direkten Nachweis zu erbringen, ob eine Argondiffusion in Kalifeldspäten stattfindet, denn man braucht nur nachzusehen, ob beim Pulverisieren von Feldspäten Argonverluste auftreten, da die Kristalle beim Zerschlagen vorwiegend an den schwachen Stellen des Kristallverbandes springen, wo sich auch das Argon ansammeln wird. Wir führten deshalb an drei verschiedenen Materialien (Mikroklin, Anorthoklas, Orthoklas) Argonbestimmungen in Abhängigkeit von der Korngrösse aus. Experimentell wurde so vorgegangen, dass jedesmal ein Stück Feldspat von etwa 300–400 g fein pulverisiert und mit Sieben die Korngrössenfraktionen gewonnen wurden. Das kleinste zur Verfügung stehende Sieb hatte eine Maschenweite von 34 μ. Die einzelnen Fraktionen unterhalb 34 μ haben wir durch sedimentieren des Materials in reinstem Aceton gewonnen. In den folgende Tabellen und Diagrammen haben wir die Messergebnisse zusammengestellt.

Die Tabellen enthalten sämtliche Messwerte, die Diagramme enthalten zur besseren Übersicht der Resultate nur die Messwerte in dem Korngrössenbereich unterhalb 100 μ.

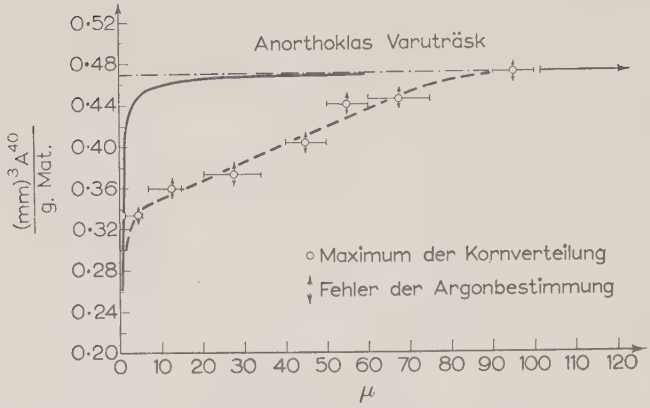

Abb. 2. Ergebnisse der Argonbestimmungen in Abhängigkeit von der Korngrösse an Mikroklin. (– – – gemessene Kurve) (—— berechnete Kurve).

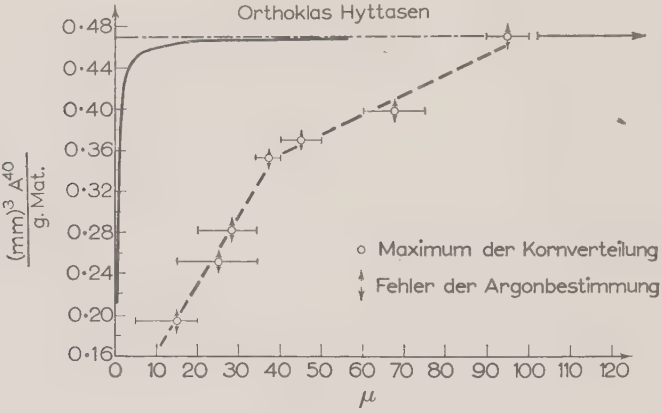

Abb. 3. Ergebnisse der Argonbestimmungen in Abhängigkeit von der Korngrösse an Anorthoklas. (– – – gemessene Kurve) (—— berechnete Kurve).

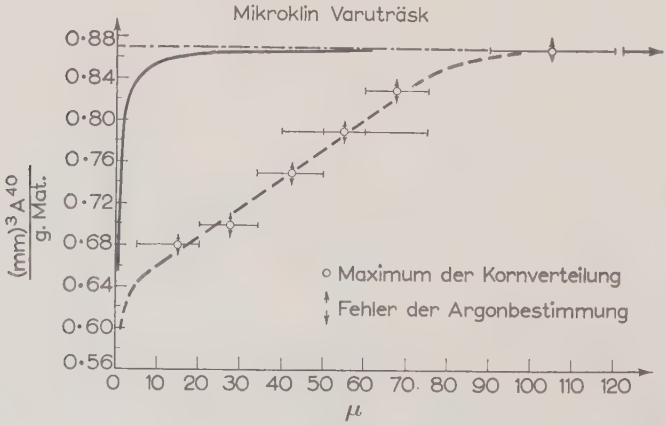

Abb. 4. Ergebnisse der Argonbestimmungen in Abhängigkeit von der Korngrösse an Orthoklas. (– – – gemessene Kurve) (—— berechnete Kurve).

In den Diagrammen haben wir auf der Ordinate den Argongehalt pro g Material aufgetragen und auf der Abszisse die Korngrösse der Feldspatkristalle. Die ausgezogene Kurve in den Diagrammen ist die berechnete Abhängigkeit des

Tabelle 2. Ergebnisse der Argonbestimmung in Abhängigkeit von der Korngrösse an Mikroklin

Material	Lfd. Nr.	Korngrösse	$\frac{mm^3 \text{ rad. } {}^{40}A}{g \text{ Material}}$
Mikroklin	71	3 — 1,6 mm	0,885
Varuträsk	90	3 — 1,6 mm	0,874
	64	3 — 1,6 mm	0,865
	74	1,6 — 1,1 mm	0,87
	76	1,1 — 0,73 mm	0,887
	75	0,73 — 0,50 mm	0,87
	80	300 — 200 μ	0,87
	98	120 — 90 μ	0,875
	91	75 — 60 μ	0,83
	93	75 — 40 μ	0,79
	72	50 — 34 μ	0,76
	73	50 — 34 μ	0,735
	92	34 — 20 μ	0,69
	96	34 — 20 μ	0,715
	101	20 — 5 μ	0,68

Tabelle 3. Ergebnisse der Argonbestimmung in Abhängigkeit von der Korngrösse an Anorthoklas

Material	Lfd. Nr.	Korngrösse	$\frac{mm^3 \text{ rad.} {}^{40}A}{g \text{ Material}}$
Anorthoklas	85	200 — 150 μ	0,474
Varuträsk	94	200 — 150 μ	0,467
	84	100 — 90 μ	0,47
	88	75 — 60 μ	0,445
	89	60 — 50 μ	0,440
	87	50 — 40 μ	0,403
	86	34 — 20 μ	0,375
	82	34 — 20 μ	0,373
	97	34 — 20 μ	0,369
	106	15 — 5 μ	0,365
	108	15 — 5 μ	0,360
	110	5 — 1 μ	0,334

Argongehaltes von der Korngrösse. Die Berechnung wurde unter der Voraussetzung durchgeführt, dass das Argon homogen im Kristall verteilt ist, und beim Pulverisieren nur diejenigen Argonatome verloren gehen, die an den neu gebildeten Oberflächen sitzen. Die berechnete Kurve ist also ein direktes Maß für die

Oberflächenzunahme bei der Pulverisierung. Wie aus den Diagrammen ersichtlich ist, weicht die berechnete Kurve unterhalb 100 μ sehr erheblich von der experimentell ermittelten ab. Der Unterschied lässt sich nur dadurch erklären, dass

Tabelle 4. Ergebnisse der Argonbestimmung in Abhängigkeit von der Korngrösse an Orthoklas

Material	Lfd. Nr.	Korngrösse	$\frac{mm^3 \text{ rad.} A^{40}}{g \text{ Material}}$
Orthoklas	100	7 — 1 mm	0,471
Hyttasen	302	7 — 1 mm	0,465
Hobol	107	100 — 90 μ	0,48
S. Norwegen		60 — 75 μ	0,398
	105	50 — 40 μ	0,372
	104	40 — 34 μ	0,353
	501	34 — 20 μ	0,283
	103	34 — 15 μ	0,252
	109	20 — 5 μ	0,195

innere Oberflächen und Korngrenzen Sammelstellen für diffundierende Argonatome sind. Für das Vorhandensein solcher innerer Oberflächen, sprechen die oben angeführten Gründe (Metamorphose und Lamellenbildung). Das Ergebnis dieser Messungen widerspricht also ganz eindeuting der bisherigen Auffassung vieler Autoren, dass Argon in Kalifeldspäten an den Gitterplätzen sitzen bleibt, wo es gebildet wurde. Bei Mikroklin und Anorthoklas (Diagramm 1 u. 2) beträgt der Argonverlust bei einer Korngrösse von 5 μ etwa 30%. Das bedeutet aber, dass mindestens 30% des gesamten Argon nicht mehr an den Gitterplätzen sitzt, wo es durch K-Einfang des ^{40}K gebildet wurde, sondern durch Volumendiffusion an eine Korngrenze oder innere Oberfläche gewandert ist. Beim Pulverisieren gingen diese Argonatome verloren und entzogen sich deshalb der Messung.

Diagramm 3 zeigt die Argonverluste eines Orthoklas in der Abhängigkeit von der Korngrösse. Bei 40μ ist ein Knick angedeutet. Wesentlich ist, dass sich der Argonverlust ungefähr 50% höher ergibt als bei Mikroklin und Anorthoklas. Dies hängt wohl damit zusammen, dass der Orthoklas in zwei Flächen leicht splatbar ist, während der Mikroklin nur eine Spaltfläche besitzt.

Das Ergebnis dieser Messungen zeigt deutlich, dass bei der Heranziehung von Kalifeldspäten zur Altersbestimmung das Material sorgfältig auf metamorphe Umbildungen untersucht werden muss. Es genügt nicht, das Material nur auf Verwitterung hin zu untersuchen, sondern es müssen von jedem Kalifeldspat, der zur Altersbestimmung herangezogen werden soll, Dünnschliffe angefertigt und diese auf metamorphe Umbildungen hin untersucht werde, da die Metamorphose im Innern der Kristalle erfolgen kann und den Kristallen äusserlich nicht anzusehen ist. Wie oben gezeigt werden konnte, hat jede metamorphe Umbildung aber Argonverluste zur Folge. Absolute Alterswerte können nur an solchen Mineralien bestimmt werden, die praktisch keine Umwandlungen erlitten haben. Die Entscheidung, ob ein Material zur "absoluten Altersbestimmung" herangezogen

werden kann, ist aber nur über eine sorgfältige mikroskopische Analyse des Materials zu treffen.

Die Untersuchungen sind durch Beihilfe der Deutschen Forschungsgemeinschaft unterstützt worden. Dr. Josef Zähringer hat freundlicherweise die massenspektrometrische Prüfung des Argon ausgeführt. Den Herren Prof. Dr. K. R. Mehnert und Dr. G. Rein sind wir für ihre geologischen Beratungen sehr zu Dank verpflichtet.

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Rare gases from the Nuevo Laredo Stone meteorite*

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Abstract—The isotopic composition of helium, neon, argon, and xenon gases from the Nuevo Laredo Stone meteorite has been measured. The concentrations of these gases have also been determined by isotope dilution, except in the case of xenon, where a less accurate method was employed. Radiogenic ^{4}He and ^{40}A are present. Cosmogenic helium, neon, and argon are present. The xenon found, which may be entirely due to contamination, was of normal isotopic composition, a fact which has a bearing on the time-interval between nucleogenesis and the formation of meteorites. The K-A age of the stone lies between 3·1 and 3·6 $\times$ 10^9 years, which establishes independently of previously published lead-isotope data for the stone that it is ancient, but suggests that there has been some loss of radiogenic argon. Most of the radiogenic ^{4}He has escaped, if a published value of the lead concentration is correct. The cosmogenic gases have isotopic compositions in general agreement with earlier work, but are present in lower concentrations, particularly so with ^{3}He. This suggests that the stone has been severely heated late in its history.

Introduction

As is now well established (Dalton *et al.*, 1953; Reasbeck and Mayne, 1955), all meteorites contain traces of radiogenic ^{4}He and cosmogenic (i.e. cosmic-ray-produced) ^{3}He and ^{4}He. Iron meteorites contain in addition traces of cosmogenic neon and argon (Reasbeck and Mayne, 1955; Gentner and Zahringer, 1955); stone meteorites contain radiogenic argon (Gerling and Pavlova, 1951; Wasserburg and Hayden, 1955; Thomson and Mayne, 1955). It is clear that there is a highly valuable rare-gas record in meteoritic matter which is just beginning to be read and which, combined with improved chemical analyses and with other isotopic studies (especially of lead), may within a few years enormously extend our knowledge of the various classes of these fascinating objects and of their origins. This paper reports on the rare-gas data obtained from a single stone meteorite, Nuevo Laredo. Using modern techniques, it has been a simple matter to obtain precise isotopic and concentration data for helium, neon, and argon, while expending only a few grams of meteorite. We have found that the stone contains all of the anomalous (i.e. non-atmospheric, isotope-wise) rare gases mentioned above.

The Nuevo Laredo Stone

This stone has been described by Patterson (1955) as a previously unrecorded find supplied by Prof. Hermion Larios of the University of Mexico. The 500 g specimen was found near Nuevo Laredo, Tamaulipas, Mexico, in 1950. It is a chondritic howardite with only a few chondrules and is classed as an achondrite. The metal content is much less than 1 per cent, and there is no evidence of oxidized iron, suggesting the absence of lawrencite. The sample had a complete fusion crust.

Patterson (1955) finds the isotopic constitution of the lead from this meteorite to be unlike that of any terrestrial lead ever examined. The abundances of the lead isotopes, relative to that for ^{204}Pb, are 50·28, 34·86, and 67·96 for ^{206}Pb, ^{207}Pb, ^{208}Pb

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respectively. If it is assumed that the present lead in this sample is a mixture of "primordial lead" as found by PATTERSON *et al.* (1953) in exceptionally uranium-free meteoritic matter (204:206:207:208 = 1:9·50:10·36:29·49) and lead generated from uranium-thorium decay, the age calculated for this meteorite is $4{\cdot}6 \times 10^9$ years. The total lead content was 0·68 p.p.m. by a method such that this figure must be interpreted as a lower limit. Corresponding lower limits for the uranium and thorium concentrations are found by calculation to be 0·2 and 0·7 p.p.m. respectively. An attempt by PATTERSON to measure the uranium concentration by isotope dilution resulted in a value agreeing with the calculated 0·2 p.p.m. within a factor of 2, and having a large enough probable error so that no discrepancy could be claimed.

METHODS

We received a clean, unoxidized fragment of the meteorite, which was crushed. The 20- to 150-mesh sieve fraction was taken for the analysis. We determined the potassium content of this material to be 0·044 per cent by flame photometry with a lithium internal standard. This is in adequate agreement with a value of 0·047 per cent K reported for the Nuevo Laredo Stone by EDWARDS (1955), who used an evaporative method for isolation of the alkalis, which were then determined by flame photometry.

For measurements of isotopic constitution, the rare gases in the stone were released by decomposing the meteorite powder in molten NaOH at 600°C for at least 12 hr. Prior to this the powder had been heated in vacuum for 12 hr at 200°C, to eliminate absorbed atmosphere gases. The vacuum system in which the work is done has been described in detail by LIPSON (1957), and embodies ultra-high vacuum techniques, so that an initial pressure less than 10^{-8} mm of Hg can easily be achieved in the system before the decomposition reaction is started. After purification of the released gases, the argon and xenon are collected in activated charcoal at liquid-nitrogen temperature and sealed off for subsequent mass-spectrometer analysis. An appreciable fraction of the helium and neon from the meteorite is sealed off in a 500 ml glass bulb attached to the purification system. The mass spectrometer measurements are carried out in an instrument especially designed for isotope abundance analyses on small noble-gas samples (REYNOLDS, 1955, 1956). During the analyses, the mass spectrometer is closed off from the pumps by vacuum valves, a procedure which heightens the sensitivity considerably in analyses of argon and lighter rare gases.

The total amounts of helium, neon, and argon present in the meteorite were determined by isotope dilution. That is, another fraction of the powdered meteorite was decomposed as before, but only after a small and known amount of an isotopic tracer of each of the rare gases had been released in the NaOH furnace. The amount of each gas originally present in the meteorite is then easily calculated from the isotopic constitution of that gas in the mixture. In the case of argon, the isotopic tracer was a sample of ^{38}A known in amount (± 3 per cent) from isotopic dilution calibration of simultaneously prepared samples. In the case of helium and neon, the isotopic tracers were samples of atmospheric composition, sealed off in a measured volume at a pressure measured with a McLeod gauge. The error in the

amounts of these tracers is judged to be less than 10 per cent. In the case of xenon only, the total amount of xenon gas present in the xenon-argon mixture was estimated from the xenon peak heights in the mass spectrometer, the run on meteorite gas being followed immediately by a run on atmospheric xenon in known amount. Possible error in this method of gas determination is considerably greater than in the isotope dilution method, but the result is thought to be valid within a factor of about 3.

Results

Table 1. Rare gases from the Nuevo Laredo Stone meteorite

Rare gas	Content in cm^3 s.t.p/g	Isotopic composition		
		36	38	40
Meteoritic argon	$1{\cdot}29 - 1{\cdot}77 \times 10^{-5}$	$\leq 0{\cdot}00092$	0.00111–0·00129	1·0000
Atmospheric argon	$\leq 0{\cdot}48 \times 10^{-5}$	(0·00338)	(0·00063)	(1·0000)
		3		4
Helium	$1{\cdot}34 \pm {\cdot}13 \times 10^{-5}$	$0{\cdot}0028 \pm 0{\cdot}0002$		1·0000
		20	21	22
Neon	$0{\cdot}90 - 1{\cdot}90 \times 10^{-8}$	$\leq 1{\cdot}0000$	$0{\cdot}58 \pm 0{\cdot}02$	$0{\cdot}60 - 0{\cdot}70$
Atmospheric neon	$\leq 0{\cdot}84 \times 10^{-8}$	(1·0000)	0·00283)	(0·0970)
Xenon	$1{\cdot}4^{+2{\cdot}6}_{-1{\cdot}10} \times 10^{-10}$	Normal ^{129}Xe not in excess by more than 1 per cent of its abundance		

Results are collected in Table 1. For argon, a pair of analyses—one with tracer and one without—is not sufficient to determine uniquely the isotopic composition and amount of meteoritic argon, since both argon samples will contain accidental or "blank" atmospheric argon in unknown and varying amounts. As a result, the number of unknowns exceeds the number of determinations. However, we found that with the data from such a pair of analyses, the quantities of interest could be fixed within rather narrow limits without making any prior assumptions about the make-up of meteoritic argon. For this argon, $0{\cdot}00111 \leq {}^{38}A/{}^{40}A \leq 0{\cdot}00129$ and ${}^{38}A/{}^{36}A \geq 1{\cdot}22$. Since for atmospheric argon, ${}^{38}A/{}^{40}A = 0{\cdot}00063$ and ${}^{38}A/{}^{36}A = 0{\cdot}186$, the meteoritic argon is clearly anomalous in composition. Gentner and Zahringer (1955) find the ratio of ${}^{38}A/{}^{36}A$ in argon from iron meteorites to be 1·7. Our lower limit for this ratio in Nuevo Laredo argon is in agreement with their

work, although the ratio could be expected to differ in the two cases, since the howarditic ^{36}A and ^{38}A is due to spallation of calcium as well as spallation of iron. The amount of non-atmospheric ^{38}A in the stone is $1{\cdot}82 \pm 0{\cdot}15 \times 10^{-8}$ cm^3 s.t.p./g. Since cosmogenic ^{40}A will be produced in amounts comparable to ^{38}A, it is clear that essentially all the non-atmospheric ^{40}A in the meteorite is radiogenic. Our limits for radiogenic ^{40}A in the Nuevo Laredo Stone are $1{\cdot}29 \times 10^{-5}$ and $1{\cdot}77 \times 10^{-5}$ cm^3 s.t.p./g respectively. The corresponding $^{40}A/^{40}K$ ratios are 0·433 and 0·594. Using the ^{40}K decay constants* consistent with a large body of data on ^{40}A in micas of known ages (i.e. contemporaneous with uraninites with concordant lead gases) (Wetherill *et al.*, 1956), we find the K-A age of Nuevo Laredo to lie between 3·09 and 3·58 billion years. This age is substantially lower than the $^{206}Pb/^{207}Pb$ age of 4·6 billion years found by Patterson, but establishes independently that the Nuevo Laredo Stone is a very ancient object.

In all of four runs the $^3He/^4He$ ratio in the meteoritic gas was $0{\cdot}0028 \pm 0{\cdot}0002$, where the large error quoted arises from the fact that the mass-spectrometer discrimination correction applicable to the mass 3/mass 4 ratio has been estimated at 6 per cent, but not checked. ^3He is about two thousand times more abundant relative to ^4He in the meteorite than it is in the atmosphere. The total amount of helium as determined by isotope dilution is $1{\cdot}34 \pm 0{\cdot}13 \times 10^{-5}$ cm^3 s.t.p./g. The error in this quantity is due only to the uncertainty in the content of the isotopic tracer, since the spectrometer discrimination is eliminated in this calculation. Since only a negligible fraction of the ^4He is cosmogenic, it is of interest to compare this value with the radiogenic ^4He content inferred from Patterson's lead data. Making the same assumptions mentioned earlier, the meteorite should contain more than $34{\cdot}8 \times 10^{-5}$ cm^3 s.t.p./g. Unless the lead concentration in the Nuevo Laredo Stone is substantially less than the 0·7 p.p.m. found by Patterson, the ^4He loss gas been considerable. ^3He is present to the extent of $3{\cdot}8 \pm 0{\cdot}5 \times 10^{-8}$ cm^3 s.t.p./g.

As determined in a single run, the relative abundances of isotopes ^{20}Ne, ^{21}Ne, and ^{22}Ne in a neon sample from the meteorite are 1·00, $0{\cdot}58 \pm 0{\cdot}02$, and $0{\cdot}70 \pm 0{\cdot}02$ Although much of the ^{20}Ne could be due to atmospheric contamination, virtually all of the ^{21}Ne must be cosmogenic. It is also definite that cosmogenic ^{22}Ne is present in amounts comparable with, but slightly greater than, the cosmogenic ^{21}Ne. The entire mass spectrometer tube was baked overnight at 370°C prior to this analysis, so that there was no background at mass 20, 21, or 22 prior to insertion of the sample. The sample was released through a charcoal trap at liquid-nitrogen temperature so at so hold back impurity gases. None of the ion peaks in the spectrometer except those due to helium, neon, and nitrogen were observed to change as a result of insertion of the sample. Reasbeck and Mayne (1955) have examined the isotopic composition of neon from an iron meteorite and find these abundances to be 1·00, 0·84, and 0·49, although they were troubled by background ions in the analysis. In both cases, however, the anomalous composition of the neon, characterized by comparable abundances at all three masses, is well established. The total amount of meteoritic neon as determined by isotopic dilution is $1{\cdot}74 \pm 0{\cdot}17 \times 10^{-8}$ cm^3 s.t.p./g assuming there to be no atmospheric contamination.

* $\lambda_\kappa = 0{\cdot}557 \times 10^{-10}$ yr^{-1}; $\lambda_\beta = 0{\cdot}472 \times 10^{-9}$ yr^{-1}.

The xenon content of the meteorite was $1{\cdot}4^{+2{\cdot}6}_{-1{\cdot}0} \times 10^{-20}$ cm^3 s.t.p./g. The isotopic composition of this xenon was identical with xenon from the atmosphere within experimental error, which was such that it was possible to establish that ^{129}Xe was not in excess by more than 1 per cent of its abundance. Thus the content of excess ^{129}Xe is less than 10^{-12} cm^3 s.t.p./g, taking the upper limit of total xenon content. Wasserburg and Hayden (1955) have discussed the importance of possible excess ^{129}Xe from ^{129}I decay in ancient meteorites as an indication of the time-interval between nucleogenesis and the formation of meteorites. They found that radiogenic ^{129}Xe was present in the Beardsley chondritic meteorite to less than $1{\cdot}3 \times 10^{-11}$ cm^3 s.t.p./g. If the iodine content was 1 p.p.m. by weight and if ^{129}I was formed initially in abundance equal to ^{127}I, their data indicate a lower limit for the time-interval of $0{\cdot}41 \times 10^9$ years. Making the same assumptions in the present case will extend this lower limit to $0{\cdot}47 \times 10^8$. All we can say about the ratio of xenon to atmospheric argon in the meteorite is that it exceeds $0{\cdot}8 \times 10^{-5}$, using the lower limit on xenon content and the upper limit on atmospheric argon content. This ratio in the atmosphere is $0{\cdot}5 \times 10^{-5}$, so that it is possible that all of the xenon examined was due to atmospheric contamination.

Discussion

As pointed out in several places above, the isotopic compositions of the rare gases from the meteorite are in general agreement with earlier work on meteorites. The concentrations of several of the gases are, however, not in agreement with earlier work.

If the lead isotopic data of Patterson and the assumptions usually made in interpreting them are accepted, 45 to 60 per cent of the radiogenic argon has escaped. If the lead concentration datum of Patterson is accepted as well, 96 per cent of the radiogenic helium has escaped. Loss of radiogenic gas to this extent is possible even without severe heating, since the parent elements potassium, uranium, and thorium are present only in trace amounts and could be concentrated at the surfaces of mineral grains where the daughter gases would be relatively mobile. For this reason, our pre-heating of the sample at 200°C may be criticized, although experience has indicated that such low-temperature heating is not sufficient to drive off a significant fraction of argon. All previous determinations of the K-A age of meteorites in which isotope dilution was used to measure the ^{40}A content (Wasserburg and Hayden, 1955; Folsinbee *et al.*, 1956) have given ages in excess of 4 billion years. Results in the range $3{\cdot}0$ to $3{\cdot}6 \times 10^9$ years have been reported, however, by workers using the more difficult and usually less accurate technique requiring quantitative recovery of argon (Gerling and Pavlova, 1951; Thomson and Mayne, 1955; Gerling and Rik, 1956).

The cosmogenic gases certainly reside for the most part within the lattices of the dense minerals comprising the stone and should not be susceptible to leakage unless heated strongly. The only prior data on cosmogenic gases in stone meteorites which have come to our attention are due to Reasbeck and Mayne (1955) on the ^{3}He content of two meteorites. For Akabar, preliminarily classified as a white chondrite, they find the ^{3}He content to be $0{\cdot}92 \times 10^{-6}$ cm^3 s.t.p./g. For Brenham

Township, they find $0{\cdot}034 \times 10^{-6}$ cm^3 s.t.p./g. For Nuevo Laredo we find $0{\cdot}038 \times 10^{-6}$ cm^3 s.t.p./g. ^{3}He, which is almost identical with the value for Brenham Township. Cherdyntsev and Abdulgafarov (1956), who have investigated the total helium content of some stony meteorites but who have not made isotopic measurements, find an anomalously high He content of about 4×10^{-3} cm^3 s.t.p./g in the meteorite Staroe Pesynoe, an achondrite of the howardite type which must be very similar to the Nuevo Laredo Stone. Chondrites which they studied contained 2×10^{-5} cm^3 s.t.p./g He or less. Our total He content for Nuevo Laredo is only $1{\cdot}3 \times 10^{-5}$ cm^3 s.t.p./g.

Comparisons with data on iron meteorites are complicated by the differences between the stone and iron meteorites when viewed as targets for cosmic-ray particles. In an attempt to see roughly how the targets differ, we have computed the number of target nuclei per gramme of howardite, relative to the number of iron nuclei per gram of iron, which are heavier than neon and which are heavier than argon. For this purpose we have taken as the chemical composition of the sample the average of seven howardite analyses tabulated by Urey and Craig (1953). Relative to iron meteorites, the nuclei which can contribute by spallation to cosmogenic neon and argon are in number 1·0 and 0·23 respectively. If the geometrical cross-sections per gramme are compared instead of the number of nuclei per gramme the ratios are 0·7 and 0·21. Calculations of this type completely ignore the dependence of the spallation cross-sections on the total mass of light particles ejected, but may be of limited validity nonetheless. For helium production, the howardite mixture of elements could be expected to be equally as effective as iron. So far as these rough considerations permit, then, the cosmogenic helium and neon content of howardites and iron meteorites could be expected to be about equal; the howardites should be poorer in cosmogenic argon by a factor of about 5.

Turning to the previous data on cosmogenic gases in iron meteorites, we find that a wide range of values are reported. Dalton *et al.* (1953), for example, tabulate ^{3}He contents for almost twenty meteorites which range from less than $0{\cdot}0002 \times 10^{-6}$ up to $8{\cdot}8 \times 10^{-6}$ cm^3 s.t.p./g. Gentner and Zahringer, (1955) reporting on four irons, find ^{3}He contents between $0{\cdot}04 \times 10^{-6}$ and $1{\cdot}73 \times 10^{-6}$ cm^3 s.t.p./g. Our value of $0{\cdot}038 \times 10^{-6}$ cm^3 s.t.p./g is within the range of values reported in both cases. However, regularities have been found by other workers in the ratio of cosmogenic neon to ^{3}He and cosmogenic argon to ^{3}He which we do not confirm. Reasbeck and Mayne (1955), reporting on three irons (four samples), find the neon/^{3}He ratio to be 0·027 with a mean deviation of less than 2 per cent. Gentner and Zahringer (1955), reporting on four irons, find the ^{38}A/^{3}He ratio to be 0·083 with a mean deviation of 16 per cent. (They were unable to determine the neon/^{3}He ratio, but found it to be less than 0·029.) In the Nuevo Laredo Stone, however, the neon/^{3}He ratio is 0·46 and the ^{38}A/^{3}He ratio is 0·48. Although the cosmogenic neon and argon contents are lower in the Nuevo Laredo Stone by about a factor of 10, the ^{3}He content is proportionately lower still, so that the neon/^{3}He and ^{38}A/^{3}He ratios are about a factor of 10 higher. It is to be hoped that more data on cosmogenic gases in meteorites by the method of isotope dilution will be forthcoming. In the meantime, comparisons of the type just made indicate that the Nuevo Laredo howardite is depleted in cosmogenic gases (especially helium) as well

as in radiogenic rare gases and, since it is quite definitely an ancient stone, we conclude that the meteorite has somehow been strongly outgassed, probably by severe heating.

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Uranium and barium in stone meteorites*

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Abstract—The uranium and barium contents of some meteorites (4 chondrites and 1 achondrite), a basalt and a dunite have been determined by neutron activation. The isotopic composition of the uranium in the stone meteorites has been shown to be the same as that of terrestrial uranium to within 10 per cent. The uranium content of the chondrites is close to $1{\cdot}1 \times 10^{-8}$ g/g; that of the achondrite (Nuevo Laredo) is about ten times higher. The barium contents are all about 350 times the uranium contents. The results are compared with previous determinations.

Introduction

The amount and distribution of uranium in meteoritic material has long been of fundamental interest in the fields comprising the earth sciences. Such knowledge is either the basis or an essential part in the understanding of time scales derived from the radioactivity of the heavy elements. It is needed to establish the heat generation in terrestrial planets. In addition it contributes to our knowledge of elemental abundances and the geochemistry of planetoids. A preliminary study of iron meteorites (Reed and Turkevich, 1955) in which radioactivation was used as the analytical tool gave results which are orders of magnitude lower than those previously reported. For this reason a general investigation of the uranium content of stone meteorites was undertaken to see if radioactivation techniques would give results in accord with those obtained by previous investigations (Davis, 1950; Chackett, Golden, Mercer, Paneth, and Reasbeck, 1950 ; Tilton, 1952; Patterson, Brown, Tilton, and Inghram, 1953; Patterson, 1955; Starik and Shats, 1956). As a byproduct of this work, barium contents of the meteorites were determined.

Experimental

Introduction. The determination of uranium in rocks using neutron activation has been investigated by groups at Oak Ridge (Mahlman and Leddicote, 1955) and Harwell (Smales, 1952). ^{239}Np and ^{140}Ba were the radioactive species sought by the respective groups. The sensitivity of the method depends, of course, on the neutron flux available; lower limits of 10^{-11} — 10^{-12} g of uranium per g of meteorite being detectable with neutron fluxes of about 10^{13} n/cm^2/sec. The fact that uranium can be determined by this method without the prior isolation of the uranium from the meteorite makes it possible to minimize the likelihood of contamination. This contamination problem is the greatest obstacle in other analytical techniques for the determination of extremely minute amounts of uranium.

The radioactivation procedure involves thermal neutron irradiation of samples of meteorite along with a monitor of meteoritic composition but spiked with microgram quantities of uranium. After irradiation the sample and monitor are dissolved in the presence of ^{237}Np and Ba carrier. The former serves as a tracer for

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.
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2·33 day ^{239}Np produced by neutron capture of ^{238}U and subsequent beta decay, and the latter as a carrier for 12·8 day ^{140}Ba produced by ^{235}U fission. The amount of uranium in the meteorite is then determined by comparing the ^{239}Np and ^{140}Ba–^{140}La activities isolated from the samples with those from the monitor. Then, on the assumption that the uranium present has normal isotopic composition, each sample irradiation gives two independent determinations of the uranium content.

The Ba isolated after irradiation contains, besides the ^{140}Ba, radioactive species induced by the interaction of neutrons with Ba present in the meteorite. These can be used to estimate the Ba content of the samples, again using the assumption of terrestrial isotopic composition for the barium.

We report here the results of the measurements of several chondrites indicating a uranium content of about 10^{-8} g/g of meteorite and one achondrite, Nuevo Laredo,* having a uranium content of about 10^{-7} g/g. In addition, a terrestrial rock of considerably higher uranium content was measured; the uranium content here agrees with that obtained mass spectrometrically by isotope dilution. The barium contents come out to be about 350 times higher than the uranium contents.

Description of samples. The experiments performed thus far have been primarily concerned with establishing the validity of the method and comparing the results obtained by radioactivation with those obtained otherwise. The meteorites selected for the most part were those for which data have been published. Whenever possible, aliquots of samples used by other workers were obtained.

Information on the samples is given in Table 1. This indicates in the first three columns the name of the meteorite, the type, and the physical character of the sample irradiated. The approximate fraction of the sample soluble in boiling 6N HCl is indicated in column 4. Column 5 indicates some sources of analytical information on the meteorite studied. Finally column 6 tells where we got the sample.

Monitors. The main consideration in preparing monitors is that the neutron intensity and energy distribution be the same in the monitor and sample. The simplest way to achieve this is to use crushed samples of meteorite spiked with a known number of micrograms of uranium far exceeding the natural content. An alternate method for preparing a monitor is to make a "mock" meteorite by preparing a solution containing the principal meteoritic constituents from the point of view of mass and neutron absorption cross section and containing a known amount of uranium. An aliquot of this solution is evaporated in a quartz tube. The equivalence of the two types of monitors was confirmed in a standard irradiation and both were used in the experiments. The chemistry was appreciably simpler in the case of the monitor prepared from the solution. Because the microgram amounts of uranium in the monitors gave higher levels of Np and Ba activity than those from the meteorite, the monitor analysis was always performed after the analysis of the meteorite samples had been completed.

A special barium monitor was used in only one irradiation. This was exposed to neutrons in two forms: one as an analysed amount of barium nitrate sealed in quartz and the other as the same amount of barium nitrate contained in a sample of Richardton meteorite. The two produced the same amount of ^{131}Ba activity. The ratio of saturation activity of ^{131}Ba per mg of barium to that of ^{140}Ba per mg of uranium, as determined in this irradiation, was used to calculate the barium contents of other samples in other irradiations.

* Patterson (1955) classifies Nuevo Laredo as an achondrite (chondritic howardite); however, a more recent publication. *A Classificational Catalogue of the Meteoritic Falls of the World*, by F. C. Leonard (University of California Press, 1956) lists this meteorite as a chondrite (olivine-clinohypersthene hypersthene chondrite).

Table 1. Samples used in uranium determinations

Name	Type	Physical character	Fraction soluble in boiling 6N HCl	References to other analyses	Source
Forest City	Chondrite	Powdered	0·29	Kunz (1890) Urey and Craig (1953)	H. C. Urey, Chicago
Modoc	Chondrite	Powdered	0·14	Merrill (1906) Urey and Craig (1953)	H. C. Urey, Chicago
Richardton (1)	Chondrite	Powdered	0·39	Quirke (1919)	H. C. Urey, Chicago
(2)	Chondrite	Fragments		Wiik (1956)	
Holbrook (1)	Chondrite	Powdered	0·15	Wiik (1956)	H. C. Urey, Chicago
(2)	Chondrite	Fragments			
Nuevo Laredo	Achondrite	Powdered	0·02	Patterson (1955)	C. Patterson, Cal. Tech.
Hualalai	Basalt	Powdered			G. Tilton, Geophys. Lab., Carnegie Inst.
Twin Sisters	Dunite	Powdered			G. Tilton, Geophys. Lab., Carnegie Inst.

Irradiation conditions. The samples (0·2–0·5 g) and monitor were sealed separately in quartz tubes which were placed side by side in aluminium cans for irradiation. All irradiations except one were carried out in the isotope tray of the Argonne CP–5 reactor. The flux was almost entirely thermal, the Cd ratio for In activation being about 2000/1, and contained approximately 10^{12} n/cm^2/sec. One sample was irradiated in the thimble of the pile where the flux was about 10^{13} n/cm^2/sec and the Cd ratio about 6/1. Irradiations lasted from three to five days.

Radiochemical yield determination. ^{237}Np, a $2{\cdot}2 \times 10^6$ year alpha emitter, was used as tracer to measure the recovery of decontaminated ^{239}Np. About 50 counts/min of the ^{237}Np alpha activity were present when the samples were being dissolved. Dissolution after irradiation was under high temperature oxidizing conditions such that all the neptunium was converted to Np^{+6}. (See details of chemistry.) Usually twenty to fifty per cent of the ^{237}Np alpha activity was eventually recovered. The 27·4 day ^{233}Pa daughter of ^{237}Np is a beta emitter and hence a correction for the growth of its activity into the Np samples was necessary. This will be discussed in the section on counting.

About 20 mg of barium were added during the dissolution of the sample as carrier for the barium radioactivities. The beta activity of this barium sample could not be used directly for the determination of ^{140}Ba because of the presence of 11·6 day ^{131}Ba. Therefore, after the lapse of several days in order to establish equilibrium, the ^{140}La daughter of ^{140}Ba was separated from the sample using cerium as a carrier (sufficiently inactive La was not available at the time). Over-all yields for the recovery of the Ba and La were 30 to 50 per cent.

Sample solution and radiochemical separations. The determining factors in selecting the chemical procedures were: (1) complete solution of the sample, (2) complete exchange between carrier or tracer and the radioactive isotope sought, and (3) high recovery.

The irradiated samples were brought into solution by Na_2O_2 fusion in the presence of carrier and tracer in a Ni crucible using about 7–8 times as much peroxide as there was sample. This

gave a nearly clear melt. After cooling, the fused mass was dissolved in dilute HCl. A small black residue sometimes remained; this was isolated by centrifugation, then dissolved in aqua regia and combined with the main solution. A drop or two of H_2SO_4 was added to the combined solutions; this was taken to dryness and then treated with dilute HCl. SiO_2 and $BaSO_4$ remained as a residue. Dehydration was necessary for otherwise Np yields were low.

Neptunium was separated from the supernatant solution after reduction with $NH_2OH{\cdot}HCl$ by coprecipitation with LaF_3. The decontamination then consisted of basic carbonate precipitations, oxidation-reduction cycles with LaF_3 precipitations, an ether extraction of Np(VI), an anion exchange step using Dowex-1 (the Np was adsorbed from a conc HCl solution 0·1 M in HNO_3, and eluted with water), and finally electrodeposition of the Np onto stainless steel discs.

Barium was separated from the silica residue by Na_2CO_3 treatment. Standard procedures (Coryell and Sugarman, 1951) were then followed to decontaminate the Ba activity. The purified barium samples in the form of $BaCO_3$ were mounted for counting on aluminium cards. The samples weighed about 15 mg and were spread over an area of about 1·5 cm^2. The cerium oxalate samples (used in the ^{140}La milking) weighed about 10 mg.

Counting. Proportional end-window counters of the flow type were used for the alpha and beta counting. The counters are operated with pure methane at 1 atmos pressure; the windows are ~0·7 mg/cm^2 rubber hydrochloride made conducting with a film of aquadag or gold (Sugarman and Haber, 1953). The counters have an alpha counting plateau of 300 V at about 2700 V and a background of about 0·1 counts/min. For beta counting a plateau of 200 V or greater exists at about 4000 V. The beta background of about 9 counts/min was stable enough to permit reliable counting down to less than 1 count/min. All samples were counted on a shelf about 2 mm from the counter window. The physical geometry at this position is approximately 40 per cent for beta particles. The counting efficiency for alpha particles was lower, about 25 per cent, probably because of air and window absorption. The counting behavior of the counters was monitored regularly using counting standards. The alpha counting reliability was checked by comparisons with measurements in a parallel plate ionization chamber.

The alpha counting was done with no covering on the sample. About 7 mg/cm^2 of Al were added to cut out the alpha particles when beta measurements were made. The ^{239}Np activity ranged from a few counts/min to about a 100 counts/min a few days after the irradiation; the ^{140}Ba activity was lower by a factor of about 10.

Decay curves were followed in order to identify the beta radioactivity. Absorption curves were also taken. The neptunium beta decay was complicated by the growth of ^{233}Pa from ^{237}Np. A master curve giving ^{233}Pa counts/min per alpha counts/min as a function of times was used to correct for the ^{233}Pa growth. After such a correction, samples decayed with the expected 2·33 day half-life of ^{239}Np. A typical beta decay curve indicating the magnitude of the correction is shown in Fig. 1.

The radiochemically pure Ba separated from irradiated stone meteorites may contain activity due to 29 hr ^{135}Ba, 39 hr ^{133}Ba, 11·6 day ^{131}Ba and the fission product chain ^{140}Ba–^{140}La. The first three arise from neutron interactions with the Ba in the original sample. The ^{140}La activity obtained in the milking experiment could be used to determine the amount of ^{140}Ba and also the contribution of the ^{140}Ba–^{140}La chain to the gross radioactivity of the Ba sample. The remainder of the long-lived activity was determined to be 11·6 day ^{131}Ba. The resolution of a typical Ba decay curve is shown in Fig. 2.

Sample purity. There are two principal sources of sample contamination. The most important and probable source is lack of complete decontamination from the very large amounts of activity in the sample. As mentioned above, decay and very often absorption curves were taken and if any contamination was indicated the samples were purified further. All data reported here are based on samples showing the right decay and absorption characteristics.

The second source of trouble, particularly in the case of very low activities, is the possibility of picking up contamination from reagents, apparatus, other samples, etc. It was found that no alpha activity had been introduced in an unirradiated sample put through the usual processing but to which no ^{237}Np was added. The chemical yield was measured by adding ^{239}Np tracer. Three similar experiments, starting with 1 g of iron wire, usual amounts of ^{237}Np tracer and barium carrier, and put through the complete procedure, gave samples having less than

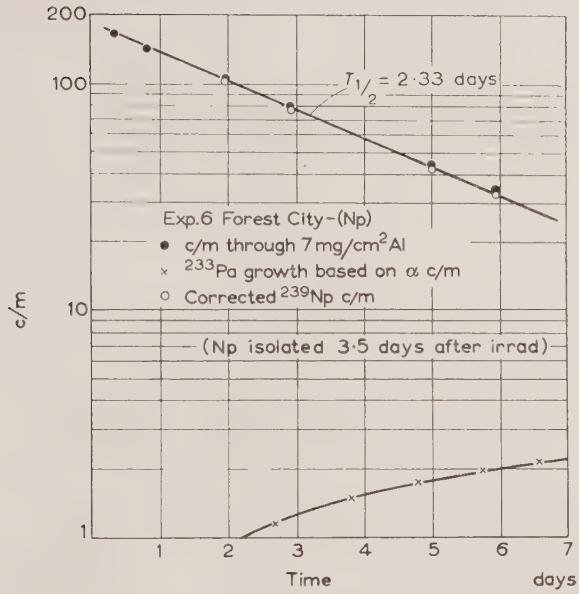

Fig. 1. Typical decay curve of 2·33 day ^{239}Np isolated from neutron irradiated meteorite. (Forest City)

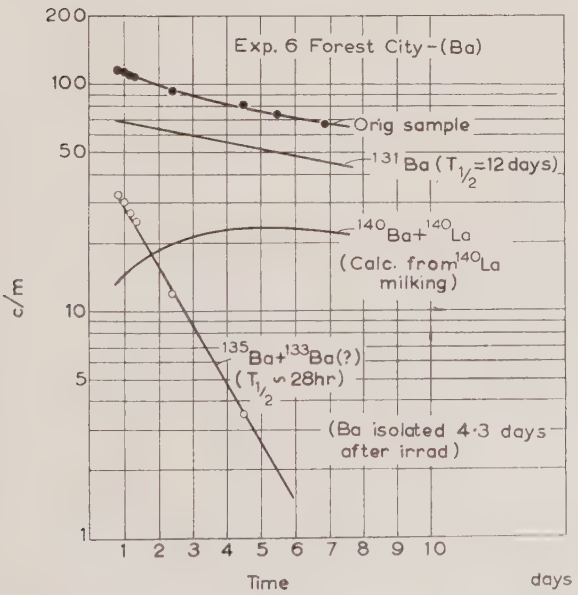

Fig. 2. Typical decay curve of barium activity isolated from neutron irradiated meteorite. (Forest City)

1 count/min of beta activity, thus indicating that the analysis normally introduced negligible amounts of activity.

A further check on sample purity is a comparison of the Np/Ba activity ratios. In a thermal

Table 2

Meteorite	U content (10^{-8} g/g)		Literature values	
	Via ^{239}Np	^{140}Ba via Ba–^{140}La	U content (10^{-8} g/g)	Reference
Chondrites:				
Forest City	(1·30)*	0·97		
	1·05	1·11 ± 0·18	6	Patterson (1955)
	0·92	1·15		
Average	0·99	1·06		
Modoc	1·08	1·08	10	Patterson (1955)
			1, 2, 2, 6	Patterson (1957)
			1·1 ± 0·2	Tilton (1952)
Richardton	1·31	1·15 ± 0·14		
	1·14 ± 0·33†	1·05 ± 0·26†		
Average	1·30	1·13		
Holbrook	1·54 ± 0·25	1·17 ± 0·24		
	1·36†	1·11 ± 0·08†		
Average	1·40	1·12		
Achondrite:				
Nuevo Laredo	12·5	12·5		
	12·0	10·8	20	Patterson (1955)
	13·2	14·0		
Average	12·6	12·6		
Minerals				
Hualalai Basalt	46·3	45·2	49·8	Tilton (1956)
Twin Sisters Dunite	0·10	0·14 ± 0·07	1·6	Tilton (1956)
	0·10 ± 0·08	0·11 ± 0·05	2·4	Davis and Hess (1949)
Average	0·10	0·12		

* The first irradiation of Forest City was performed in the thimble of the pile where resonance neutrons may have enhanced the activation of ^{238}U.

† The second irradiations of Richardton and Holbrook were of uncrushed fragments of the meteorites.

flux this ratio is dependent on the fission to absorption cross sections, the relative counting efficiencies and the isotopic composition. The theoretically expected $A^{\infty}_{Np}/A^{\infty}_{Ba}$ is about 10; that observed in this series of experiments was constant and equal to 10 for both monitors and samples to within the experimental fluctuation of 10 per cent.

Neutron shadowing. Sample self-shadowing was expected to be negligible for the small amounts used. An irradiation was carried out using monitors weighing 0·33, 0·69, 1·30, and

2·61 g and all having 5·8 micrograms of uranium/gram. The amount of both Np and Ba activity produced was found to be proportional to the uranium content in all but the heaviest sample. This showed a possible 14 per cent self-shadowing effect. The monitors used in the analyses had at most 3 micrograms of uranium.

Results

The results on the uranium content of samples analysed to date are presented in Table 2. The first column describes the sample, the next two give the uranium content deduced via the ^{239}Np and the fission product mass 140 chain, respectively. The different numbers in a given column are the results of separate irradiations. The last two columns indicate the results of previous work on the same samples.

In general, the standard errors to be assigned to the individual entries should be taken as less than 10 per cent. In the cases where particularly low counting rates were encountered, appropriately higher errors are indicated in the table. The averages have been computed by suitable weighting.

The uranium contents show an agreement from one experiment to another consistent with the errors of the method. In addition, the results from the Np and fission product mass 140 chain agree within these errors. It is thus unlikely that the isotopic composition of the uranium in these stone meteorites is appreciably different from that found terrestrially. Our data indicates less than 10 per cent difference. This is in agreement with a determination by Schumb, Evans and Hastings (1939) on the meteorite Pultusk which had lower accuracy than the present work. The recent results of Petrzhak *et al.* (1956) likewise showing a normal composition of meteoritic uranium presumably refer to samples extracted by a technique that gives uranium contents an order of magnitude higher than the one reported here (see below).

The uranium contents of the four chondrites (Forest City, Modoc, Richardton, and Holbrook) are very similar and equal to $1{\cdot}14 \times 10^{-8}$ g/g. The single achondrite investigated, Nuevo Laredo, shows approximately ten times more uranium ($12{\cdot}6 \times 10^{-8}$ g/g).

The uranium content obtained here for the meteorite Modoc agrees very well with that reported by Tilton (1952) based on an isotope dilution determination. The present results are definitely lower than Patterson's (1955) published estimates for the meteorites Forest City and Modoc, and somewhat lower than these authors deduce for Nuevo Laredo. These estimates were based on the amounts of uranium required to produce, over the last four and a half billion years, the radiogenic ^{206}Pb and ^{207}Pb found in the meteorites today. Patterson's (1957) recent isotope dilution measurements on the uranium content of Modoc give values between 1 and 6×10^{-8} g U/g and are in better agreement with our results.

The adequate agreement between our uranium value and that of Tilton (1956) for the basalt suggests that when the uranium content is high ($>10^{-7}$ g/g) contamination problems in other methods of uranium determination are minimized. The comparison of our results on stone meteorites with those of other workers supports this (see above) as does the large discrepancy in the case of the dunite. Our number for the dunite ($0{\cdot}11 \times 10^{-8}$ g/g) is about twenty times lower than those of Tilton (1956) or Davis and Hess (1949). It is however, in accord with the results of

Davis (1950) on the silicate phase of pallasites. The mineral composition here is similar to that of dunite.

The ^{131}Ba activity in the purified barium samples was obtained by subtracting the ^{140}Ba–^{140}La contribution as established by the La milking from the gross barium activity. This difference was then used as a measure of the natural barium in the irradiated sample. The results are given in Table 3. The table lists in three columns the meteorite, the result obtained in separate irradiations for the barium content, and, finally, comparable literature data. A larger scatter in these results is not unreasonable because of the indirect way in which the ^{131}Ba contribution was established and because the nature of the radiations of ^{131}Ba make the measurements very sensitive to counting conditions. In addition, again because of the various contributions to the beta activity, the usual criteria for radiochemical purity—absorption and decay curves—could not be used effectively. Again the four chondrites appear to have very similar barium contents—3–4 p.p.m.—while the achondrite (Nuevo Laredo) is about ten times higher. Comparison with the few determinations in the literature that can be made (column 3) indicates only

Table 3. Barium content of meteorites

Meteorite	Barium content (10^{-6} g/g)	Literature
Forest City*	3·2	9 (Pinson *et al.*, 1953)
	4·1	
Average	3·7	
Modoc	3·6	
Richardton	3·4	
	3·0	
Average	3·2	
Holbrook	4·7	3–10 (Von Engelhardt, 1936)
	3·2	9 (Pinson *et al.*, 1953)
Average	4·0	
Nuevo Laredo	56	
	39	
	42	
Average	46	
Minerals		
Hualalai Basalt	310	
Twin Sisters Dunite	0·30	7 (Pinson *et al.*, 1953)
	0·48	
Average	0·39	

* The barium sample from one irradiation of Forest City was contaminated and did not give a trustworthy result and so is not included.

moderate agreement in the case of the meteorites Forest City and Holbrook. Our result on the dunite (0·4 p.p.m.) is significantly lower than the value of 7 reported by Pinson *et al.* (1953). Von Engelhardt (1936), however, has found that the barium in two South African dunites as well as in three Norwegian olivine samples was below his limits of sensitivity (1 p.p.m.). These latter results are in accord with our observations on Twin Sisters dunite.

There appears to be a definite correlation between the barium and the uranium contents of the samples analysed here. Thus the concentration of individual elements vary by a factor of more than 400 whereas their ratio in the samples varies by less than a factor of three. Within the meteorite group the variation appears even less and the barium content is about 350 times the uranium content.

Discussion

As pointed out above, the uranium content of the four chondrites (Forest City, Modoc, Richardton, and Holbrook) is the same within our errors and averages about $(1{\cdot}14 \pm 0{\cdot}12) \times 10^{-8}$ g/g. Of other published data on chondrites the values for Akaba (Reasbeck and Mayne, 1955) and Cumberland Falls (Davis, 1950) are 0·8 and $1{\cdot}0 \times 10^{-8}$ g/g, and are thus in essential agreement. Other values such as the 11 for Beddgelert (Chackett, Golden, Mercer, Paneth, and Reasbeck, 1950) and the recently reported values of Starik and Shats (1956) on three chondritic meteorites are ten to twenty times higher. The latter authors also got much higher uranium contents for iron meteorites than did Reed and Turkevich (1955). We base our confidence in the validity of our results on the greater insensitivity of our technique to contamination, to the agreement of the results obtained via ^{140}Ba and ^{239}Np with their very different chemistry, and to the check of the activation technique (Hualalai Basalt) by the isotopic dilution method when the concentrations are high enough to minimize the effect of contamination in the latter. Our opinion is, therefore, that the chondrites do have a relatively constant uranium content equal to about 10^{-8} g/g.

The single achondrite studied in this work, Nuevo Laredo, shows not only a higher uranium content (13×10^{-8} g/g), but also has different amounts of other minor constituents such as Pb (Patterson, 1955), Na and K (Edwards, 1955), rare gases (Reynolds and Lipson, 1956), and Ba (see above) than typical chondrites. On the other hand, reported uranium contents of other achondrites show varying amounts (1, 5, and 6×10^{-8} g/g) (Patterson *et al.*, 1953; Davis, 1950; Van Dijk, De Jager, and Demetter, 1953).

Following the procedures of Suess and Urey (1956) to calculate the cosmic abundances of the elements from the composition of chondrites leads to a value for uranium of $7{\cdot}8 \times 10^{-3}$ atoms of ^{238}U for every 10^6 atoms of Si. This is close to the abundance surmised by Patterson *et al.* (1953). Uranium is thus the least abundant of all the elements known to have stable or long-lived isotopes, and was so even $4{\cdot}5 \times 10^9$ years ago. In view of the present uncertainties in the cosmic abundances of Pb, Hg and Tl, it is not clear whether the general abundance curve drops rather sharply above mass 208, or whether there is a gradual decrease starting with the platinum group at about mass 195. The platinum group elements have abundances

a hundred times greater than the value deduced here for uranium. Acceptance of our value for the uranium content of chondrites would appear to solve satisfactorily the problems connected with the heat balance of the earth, the moon and Mars that have been emphasized by UREY (1952, 1955, 1956).

Our average value for the barium content of chondrites (~4 p.p.m.) appears to confirm SUESS and UREY's (1956) choice of ~4 p.p.m. in disregard of PINSON's measurements leading to an average of 8 p.p.m.

It is important to examine the bearing of these uranium determinations on the meteoritic ages deduced by PATTERSON (1956) from lead isotopic ratios. The fact that we find less uranium than is needed to produce these isotopic ratios and the absolute amounts of lead as measured by PATTERSON (see Table 2) can be explained in one of three ways. Since the determinations were not performed on the identically same samples, there could be variation in abundance of these minor constituents of meteorites. This could be the cause of the discrepancy in Nuevo Laredo where less than a factor of two is needed. The explanation could lie in a history of the meteorite such that the ratio of lead to uranium varied with time. Finally, either the lead or the present uranium experiments may be at fault. For example, the presence of contamination in the work of PATTERSON could lead to high results.

The lead isotopic ratios of Nuevo Laredo are so abnormal and the discrepancy in absolute amounts is small enough so that it is hard to conceive of a contamination mechanism that would materially alter the deduced age of $4{\cdot}55 \times 10^9$ years. The situation is much more serious in the cases of Forest City and Modoc. Here, interpretation of the discrepancy in terms of the most obvious type of contamination (by terrestrial lead) would practically destroy the usefulness of the lead isotope data for age determinations for these meteorites.

In view of recent (CAMERON 1956; BURBIDGE *et al.*, 1956) interest in neutron capture processes in stars, it is perhaps worth pointing out that the fact that the uranium in stone meteorites has the same isotopic composition (to within 10 per cent) as does terrestrial uranium argues strongly for the ^{235}U and ^{238}U in meteoritic matter having had essentially the same history as regards exposure to neutrons as did terrestrial matter. The neutron destruction cross sections of ^{235}U are known (HUGHES and HARVEY, 1955) to be at least a factor of five higher than those of ^{238}U at energies above 10 keV and probably even below this energy. Any significantly different exposure to neutrons would therefore have distorted the $^{235}U/^{238}U$ ratio from that prevailing terrestrially.

Strictly speaking, the analysis for ^{140}Ba is really an analysis for any heavy nuclide fissionable with thermal neutrons (the fission yield of ^{140}Ba does not vary appreciably in slow neutron fission of many nuclides). Interpreted in this way, our results indicate that the sum of the products of thermal neutron fission cross section in barns for all heavy nuclides times the weight in grams is $4{\cdot}7 \times 10^{-8}$ g barns per gram of chondritic meteorite. We interpret this number to indicate normal isotopic composition for the uranium in the meteorites; this would mean that all fissionable nuclides other than ^{235}U contribute less than 10 per cent to this product. Concretely, it sets limits of the order of 10^{-10} g/g for the concentration of nuclides such as ^{239}Pu or ^{247}Cm (DIAMOND, FRIEDMAN, GINDLER, and FIELDS, 1957) in chondrites.

Acknowledgements—In conclusion we should like to acknowledge our debt to Dr. H. C. Urey, who early emphasized the need for new analyses for uranium in meteoritic matter, and provided continual stimulus for the work. Dr. Urey, Dr. C. C. Patterson, and Dr. G. Tilton are to be thanked for help in obtaining the samples; Dr. S. G. English of the U.S. Atomic Energy Commission kindly made available the ^{237}Np tracer used here.

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LETTERS TO THE EDITOR

Chemical energy and metamorphism

(*Received* 8 *February* 1957)

An article with the above title has been published in *Geochimica et Cosmochimica Acta*, **8**, 86–107, 1955, which was written by V. A. Saull of the Massachussetts Institute of Technology.

In his article, V. A. Saull is discussing an idea "that the chemical energy of metamorphism is solar energy which has been stored during rock-weathering." His article is based upon the use of the thermochemical data.

In the U.S.S.R., however, the same idea was advanced as early as 1946 by V. I. Lebedev* (Leningrad University) and by N. V. Belov† (Moscow, Institute of Crystallography). To prove their idea, the authors made use of the crystal-energy data, obtained by comparison of the distances and character of the bond between Al and O when Al has different co-ordination numbers (Al in co-ordination 4 with the distance Al – O = 1·6–1·75 Å is characteristic for the minerals of the eruptive rocks, and Al in co-ordination 6 with Al – O = 1·8–2·0 Å is characteristic for the minerals of sedimentary rocks).

Some time later this hypothesis was discussed in a number of papers:

V. I. Lebedev (1948) On the question of the ways of developing of the Soviet mineralogy and on the problem of the energetics of the silicates. *Věstnik Leningrad University* No. 11.

N. V. Belov (1951) A Speech. Transactions of the first conference on the questions of cosmogony. *Acad. of Science U.S.S.R.*

N. V. Belov (1952) Geochemical Accumulators. Transactions of the Institute of Crystallography. *Acad. of Science U.S.S.R.* No. 7.

V. I. Lebedev (1953) One probable source of force of the tectonic movements in the earth's crust. *C. R. Acad. Sci. U.R.S.S.* **90,** No. 2.

V. I. Lebedev (1953) On the problem of accumulation of the solar energy by the crystalline matter of the earth. *Acad. of Science U.S.S.R.*

V. I. Lebedev (1954) On the possibility of absorption of solar energy by the crystalline matter of the earth *Izv. Akad Nauk. S.S.S.R. Ser. geol.* No. 4.

It must be added that for supplementary data V. I. Lebedev uses the main thermochemical evidences, which are also used by V. A. Saull. The idea advanced by us has been criticized.

V. S. Sobolev (1947) The meaning of the co-ordination number of aluminium in silicates. Mineralogical Symposium No. 1.

D. S. Korzhinsky (1955) The exaggeration of the role of the solar energy in the energetics of the earth's crust. *Izv. Akad. Nauk. S.S.S.R., Ser. geol.* No. 1.

It is clear from the above statement that in the U.S.S.R. the idea of the accumulation of solar energy was introduced a long time ago and has been studied ever since, although V. A. Saull does not mention it in his article.

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* Lebedev V. I. (1946) On the problem of raolinite nucleus. *C. R. Acad. Sci. U.R.S.S.* **51,** No. 1.
† Belov N. V. (1946) X-rays and the composition of crystals. *Izv. Akad. Nauk. S.S.S.R. Ser fiz.* **10,** No. 4.

Chemical energy and metamorphism

Reply to Letter from V. I. Lebedev and N. V. Belov

I am grateful to Dr. Earl Ingerson, American editor of *Geochimica et Cosmochimica Acta*, for the opportunity to comment on the above letter.

In the summer of 1956, I received a similar letter from Prof. Lebedev, asking in addition what further work I had done. In my reply, I expressed my interest in the Russian work, and stated that I desired to study in detail the references cited before discussing our relative concepts. My thought was to submit a note to *Geochimica et Cosmochimica Acta* on my findings, but a preliminary statement now seems called for.

The work on which my paper is based was entirely independent. To my best recollection, my first specific interest in the problem dates from the fall of 1949. At that time, I began to develop the subject as my Ph.D. thesis, and the degree was awarded in early June 1952.

Very careful library work was done in preparing this thesis, particularly because of the fundamental nature of the conclusions developed. No prior mention of the principal concept, or even of the general problem investigated, was found, nor do I think that any reasonable search would have uncovered whatever Russian work there had been. I believe this is apparent from the following.

No reference to the theme of my paper appears in any of the Russian titles cited before the late 1952 Belov reference. Neither do the abstracts of the 1946 papers of Lebedev and Belov (*Chemical Abstracts* 7091^{6} (1946); 8628^{h} (1948); *Mineralogical Abstracts* **10,** 23 (1949)) contain any mention of this theme. No abstracts of the references Lebedev (1948) or Belov (1951) are given in *Chemical Abstracts* or *Mineralogical Abstracts*, nor have any been located elsewhere. These facts, coupled with the study I have made to date of the references themselves, indicate that my thesis work was the first definitive treatment of the problem. The *Geochimica et Cosmochimica Acta* paper was entirely based on part of this thesis, with no modifications or additions whatsoever.

Concerning this paper, the references given include only those works actually consulted by me, and in this sense the list is complete. However, I now realize that a bibliography of the subject at that time should have included the Russian references of 1952 and 1953. The *Geochimica et Cosmochimica Acta* paper was prepared for publication in December 1954, and a thorough search of the literature since 1952 was not made. This was an oversight, and my only justifications for it are that there had been no whisper of similar work found in my earlier search, and that the chemical theory, experimental data, and field data on which my paper is based had been in the literature for more than twenty years. No new experimental work was required to arrive at the principle formulated.

The Russian approach, at least prior to the Lebedev (1954), paper has to my knowledge been via qualitative crystal-energy studies based upon interionic distances. I considered the advisability of this approach in some detail while working on my thesis, and concluded that it would be unlikely to yield convincing arguments, on a broad front, within the time available to me. My own approach has been via thermochemistry, which I still consider is the only approach that will yield unequivocal results. Lebedev's later references do make use of thermochemical data, but there has been no attempt at a complete treatment.

In conclusion, I wish to make it clear that I find the Russian support for the ideas set forth in my paper gratifying, and hope that our joint work will stimulate more active study of this most fundamental problem. I hope to discuss the Russian contribution more fully in a separate paper, and to have the pleasure of corresponding personally with Messrs. Lebedev and Belov.

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SOME CURRENT PAPERS IN OTHER JOURNALS

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Crust of the Earth (Symposium). Arie Poldervaart, ed. New York 1955. (A. B. Ronov and V. E. Khan).

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Book reviews

GMELIN-INSTITUT, Clausthal-Zellerfeld. **Gmelins Handbuch der anorganischen Chemie, 8. Auflage. System Nummer 32: Zink**. Ergänzungsband. Verlag Chemie, Weinheim/Bergstr. 1956. 1025 S. mit 191 Abb. Preis: Kartoniert DM 570, Ganzleinen DM 575.

DER neue Band von Gmelins Handbuch der anorganischen Chemie ist ein Ergänzungsband, der alle Nachträge für den 1924 erschienenen Hauptband Zink bringt. Im allgemeinen sollte nur die Literatur von 1924-1949 zusammengestellt werden, es kann aber mit Befriedigung festgestellt werden, dass jedenfalls in dem Teil *Geochemie* Arbeiten bis 1956 berücksichtigt worden sind. Dieser Teil *Geochemie* umfasst 77 Seiten, dazu kommen 2 Seiten über das Vorkommen in Gestirnen und Meteoriten. Es schliessen sich an die topographische Übersicht mit 40 Seiten und auf 18 Seiten ein Überblick über die Zink-Minerale. Diesem ganzen Vorkommensteil mit 136 Seiten waren im ersten Band nur 10 Seiten gewidmet. Diese 136 Seiten sind für den Geochemiker besonders wichtig, insbesondere die eigentliche Geochemie, in der sehr viel neues Material zusammengetragen worden ist. Von den weiteren Teilen des umfangreichen Werkes dürfte für die Leser dieser Zeitschrift besonders das Kapitel über die Verbindungen des Zinks, Seite 770-1025, von Interesse sein, so die dem Zinksulfid gewidmeten 31 Seiten.

Bei dem ausserordentlich hohen Preis des in allen Teilen wichtigen und nützlichen Werkes wird doch mancher Geochemiker bedauern, dass nicht einzelne Teile für sich bezogen werden können.

C. W. CORRENS

D. K. KRYNINE and W. R. JUDD: **Principles of Engineering Geology and Geotechnics.** McGraw-Hill, New York, 1957. 700 pp. $10.00. £3 15s.

IN RECENT years engineering geology has been recognised as a discipline in its own right. Geotechnics, or as we say in England, geotechnology, has appeared quite recently and it must be confusing to many civil engineers to attempt to define the border line between these subjects. In their new book Messrs. KRYNINE and JUDD have found it necessary to add a subtitle—*Geology, Soil and Rock Mechanics and Other Rock Sciences as Used in Civil Engineering.*

As the title implies, this book is a text book, not a collection of case histories with detailed accounts of construction techniques. The first eight chapters consist of geotechnical information of a general character applicable to any structure, not summaries of geology and geomorphology.

In the first chapter the authors deal briefly with mineralogy and petrology from a quite practical point of view, e.g. the tabular classification of the igneous rocks is on the basis of colour and texture. There is a similar textural classification of the sedimentaries. The authors have also not been afraid to describe briefly the clay minerals in a fundamental way.

The somewhat unusual feature of the book is the treatment of structural geology. Here structures have been treated in the chapter on the engineering properties of rocks, as mechanical deformations of the rocks. This approach would seem to be more appropriate than a list of the structures which can be found in nature.

Geomorphology finds its place in Chapter three, *Formation and Engineering Use of Soils.* with an understandable bias towards the kind of environment found in the United States, In particular the properties of loess are covered in some detail.

It was expected that the chapter on soil mechanics would be of a high standard although of a very elementary and general nature.

The remaining chapters of a general nature are on *Subsurface Water, Subsurface Exploration, Maps and Air Photo's* and *Rock as a Construction Material.* The chapter on maps and air photos

is a valuable exposition of a technique of geological surveying which is growing in importance.

The last 350 pages in the book are devoted to chapters covering the application of geotechnical principles to particular civil engineering problems. Of special interest are the chapters on frost and permofrost and aseismic design, subjects about which information and experience are not readily available in England.

The chapter on tunnelling is a welcome summary of the most up-to-date techniques, and covers such devices as roof bolting.

Much of the material contained within the later chapters is, however, not strictly engineering geology and encroaches into the subjects of foundation engineering, dam engineering and construction work in general.

This book can be recommended to undergraduates in both civil engineering and geology since the authors do not hesitate to define the simplest terms. Practising engineers will find it useful in giving them an insight into the principles behind the specialist services which they may be called upon to use.

Although the authors have attempted to make the definition of their subject broad, that virtue has had to be paid for and it is not easy to find a clear underlying theme throughout their work except the very general one of the application of the earth sciences to civil engineering.

The book is well printed with numerous illustrations and photographs. There is a tendency, common in books of this kind, to present drawings with far more detail than the text warrants.

A common American practice is followed in that material which need not be studied on first reading is printed in a smaller type.

A notable feature of the book is the lists of references at the end of the chapters.

Bryan O. Skipp

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